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The Institution as a body is not responsible for the statements of opinion expressed in any of its publications.

Copyright.—Publication of abstracts of Papers and articles appearing in the Journal is permitted, provided that acknowledgment is made to the Institution of Petroleum Technologists.

Papers and Articles.—The Council invites Papers and Articles both for reading at Ordinary Meetings of the Institution and for publication in the Journal. All Papers, whether for reading or publication, will be submitted to a referee appointed by the Publication Committee.

The Institution has published a brochure "Instructions for the Guidance of Authors" containing details of recommended practice in the preparation of Papers for publication. Copies of this brochure will be supplied on request.

Pre-Prints.—Advance proofs of Papers to be read at Ordinary Meetings are generally available about a week before the Meeting. Members wishing to be supplied with these pre-prints are requested to notify the Secretary.

Abstracts.—Members and Journal Subscribers desirous of receiving the Abstracts printed on one side of the paper only, can be supplied with these at a charge of 10*s.* per annum per copy, payable in advance.

Issue of Journal.—Members whose subscription is not in arrear receive the Journal free of cost. A member whose subscription is not paid by March 31st of the year for which it is due is considered to be in arrear.

Changes of Address.—Members are requested to notify any change of address to the Secretary.

Benevolent Fund.—The Benevolent Fund is intended to aid necessitous persons who are or have been members of the Institution, and their dependent relatives.

The Fund is raised by voluntary annual subscriptions, donations, and bequests, and all contributions should be sent to the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2. The Fund is administered by the Council through the Benevolent Fund Committee, and all applications in connection therewith must be made on a special form which can be obtained from the Secretary of the Institution.

Appointments Register.—A register of members requiring appointments is kept at the offices of the Institution, and every effort is made to assist members of the Institution in search of employment.

Members who desire their names and qualifications to be included in this register are requested to apply to the Secretary for the Form of Application for Registration, if they have not already done so. Members residing in the London area are asked, if possible, to return this Form in person and make themselves known, together with their requirements, to the Secretary. It is also requested that members should notify the Secretary immediately they have obtained an appointment.

In submitting names of candidates to prospective employers it is understood that the Institution accepts no responsibility and gives no guarantee.

Library.—The Institution's Library may be consulted between the hours of 10 a.m. and 5.30 p.m. daily. (Saturdays, 10 a.m. to 12 noon.)

GENERAL MEETINGS.

General Meetings of the Institution will be held on the second Tuesday in each month at 5.30 p.m. at the Royal Society of Arts, John Street, Adelphi, London, W.C. 2.

Tea, coffee and light refreshments will be provided at 5.0 p.m. prior to each meeting.

Members may introduce visitors.

Feb. 12*th*. **"The Petroleum Geology of Western Canada."**
A. J. Goodman, B.Sc., A.M.Inst.P.T.

Mar. 12*th*. **Annual General Meeting and Induction of New President.**

April 9*th*. **"The Boundary Friction of Oxidised Lubricating Oils."**
Dr. E. R. Redgrove, Ph.D., B.Sc., M.Inst.P.T.

May 14*th*. **"Drilling Muds."**
P. Evans, F.G.S., A.M.Inst.P.T., and A. Reid, A.M.Inst.P.T.

INFORMAL DINNERS.

An informal Dinner is held at Gatti's Restaurant, King William Street, Strand, W.C. 2, immediately following each General Meeting of the Institution, to entertain the speaker of the evening.

A very cordial invitation is extended to all Members of the Institution.

The cost of the Dinner is 5*s*. (exclusive of wines). No separate notification of these Dinners will be issued.

STUDENTS SECTION.

(London Branch.)

Meetings of the Students Section (London Branch), unless otherwise notified, will be held at the Institution offices at 6.15 p.m. on the dates specified below.

Feb. 5*th*. **"Determination of Cloud Point of Black Oils."**
J. W. Hyde (Student).

Feb. 19*th*. Annual General Meeting.
"Efficiency of Modern Distillation."
R. H. Keach, B.Sc. (Student).

Feb. 28*th*. Visit to The Gas Light & Coke Co., Beckton Works.
Annual Dinner.

Mar. 8*th*. **"The Structural Conditions of Oil Accumulation in Europe."** Symposium.

Mar. 22*nd*. **"Health Hazards in the Petroleum Industry."**
J. McConnell Sanders, F.I.C., F.C.S. (Vice-President).

May 7*th*. **"Crooked Holes."**
A. J. Haworth (Student).

May 21*st*. To be announced later.

Tea and light refreshments will be provided at 5.30 p.m. prior to each meeting.

The Committee of the Students Section extends a cordial welcome to all Members of the Institution to attend the meetings of this Section.

NEW MEMBERS.

The following have been elected or transferred, subject to confirmation in accordance with By-Laws, Sect. IV, paras. 14–15, since the last issue of the Journal.

Members.

Meherin, John B.	Burma.
Robinson, James Terence Trimble	Trinidad.
Vincent, John Willford	Stanford-le-Hope.
Ward, Harry L.	Punjab.

Transferred to Member.

Keith, Hugh	Barbados.

Associate Members.

Cooper, Arundel David	London.
Evans, John Trevor	Upper Burma.
Smith, Maxwell	London.

Students.

Catchpole, William Marcus	Teddington.
Groves, Philip Ernest	Dartford.
Hitchcock, Norman Ernest Frederick	Southall.
Jackson, James	London.
Kirby, Harold Evans	Teddington.
Lorne, Henry Thomas	London.
Maling, Peter Bromley	London.
Martin, Rex Ingram	St. Albans.
Purdie, Andrew Clark	Folkestone.
Young, Raymond Owen	London.

Associates.

Blackwell, William	Birmingham.
Blake, Donald Murray	Chigwell.

NOMINATIONS FOR MEMBERSHIP.

The following nominations for membership of the Institution of Petroleum Technologists were approved by the Council on 8th January, 1935, and the application forms may be seen at the offices of the Institution.

The names of the Proposer and Seconder are given in parentheses.

As Members.

Bihoreau, Charles, Directeur des Services techniques de l'O.N.C.L. 85, Boulevard du Montparnasse, Paris. (L. Pineau; J. A. Lautier.)

Frischknecht, Dr. Gustav, Geologist, c/o Trinidad Leaseholds, Ltd., Pointe-a-Pierre, Trinidad, B.W.I. (H. G. Kugler; E. C. Scott.)

Knighton, Charles William, Engineer, "Langley," Townsend Avenue, Old Southgate, London, N. 14. (J. Kewley; R. B. Grey.)

Melvill, Francis Leopold, Chemical Engineer, c/o Trinidad Leaseholds, Ltd., Pointe-a-Pierre, Trinidad, B.W.I. (H. G. Kugler; E. C. Scott.)

As Associate Members.

ANANTHANARAYANAN, K. S., Assistant Petroleum Chemist, Asiatic Petroleum Co. (S.S.) Ltd., Pulo Bukom, Singapore. (L. H. Cooper; E. R. Cartwright.)

BOOTH, Donald Bartleman, Engineer, "The Homestead," Mount Pleasant, Cockfosters, Herts. (J. S. Jackson; A. M. E. Beavan.)

GRAY, George Edward, Technical Director, Silene Lubricants, Ltd., St. Silas Street, Hull. (J. R. Smellie; E. A. Evans.)

WASSELIN, Pierre Charles, Chemical Engineer, Cercle des Ingenieurs a l'Avera, par Martigues (Bouches du Rhone), France. (M. E. Hubbard; A. F. Strickland-Constable.)

As Transfer to Associate Members.

KELLY, Michael Everitt, Chemist, c/o Anglo-Persian Oil Co., Ltd., Abadan, Persian Gulf. (A. W. Nash; L. V. W. Clark.)

FFOULKES-JONES, Rogers Garson, Exploitation Engineer, c/o United British Oilfields of Trinidad, Point Fortin, Trinidad, B.W.I. (H. W. Reid; C. Capito.)

As Student.

MENDELL, Wilbert Thornton, Student, Imperial College Hostel, Prince Consort Road, South Kensington, London, S.W. 7. (V. C. Illing.)

THE JOURNAL.

Commencing with the present issue of the *Journal* the size of page has been increased from Demy Octavo ($8\frac{1}{4}'' \times 5\frac{1}{4}''$) to $9'' \times 6''$. The latter size was agreed upon by the Council after very thorough examination of all the relevant factors of cost, transmission by post, convenience of handling and storing particularly under field conditions, binding, etc.

Concurrently with the change in size various minor alterations have been introduced. The Table of Contents has been printed on the front cover. The Preliminary Section has been re-named "Institution Notices" and will be utilised to a greater extent than formerly for keeping members informed of events of interest to the Institution. Book reviews and notices of books received have been transferred to the Abstracts Section. Various modifications have been made in typography and arrangement.

The Council and Publication Committee are desirous only of providing a *Journal* which meets with the general approval of the members, and would welcome any expression of opinion on the new format, or any suggestions for the further improvement of the *Journal*.

VICE-PRESIDENTS, SESSION 1935–36.

The Council have elected the following as Vice-Presidents for the Session 1935–36: Lt.-Col. S. J. M. Auld, Ashley Carter, C. Dalley, Prof. A. W. Nash, J. McConnell Sanders and Dr. F. B. Thole.

SUMMER MEETING AND ANNUAL DINNER.

A Summer Meeting of the Institution will be held in London on Friday, 28th June, 1935. Further details of this meeting will be announced in a subsequent issue of the *Journal*, but it is proposed to devote two sessions to the discussion of the Annual Reports on the Progress of Naphthology.

The Annual Dinner will be held at the Park Lane Hotel on the evening of Friday, 28th June.

JOINT MEETING WITH INSTITUTION OF AUTOMOBILE ENGINEERS.

A Joint Meeting will be held with the Institution of Automobile Engineers and other Technical Societies on Tuesday, 5th March, 1935. The subject for discussion is "Cold Pressing and Drawing." Two Papers will be presented by Dr. H. Gough, D.Sc., F.R.S., and Dr. C. H. Desch, D.Sc., F.R.S., dealing with the subject from the mechanical and the metallurgical point of view respectively.

The Meeting will be held in the Hall of the Royal Geographical Society, Kensington Gore, S.W. 7, at 7 p.m. The Chair will be taken by Sir Harold H. Carpenter, M.A., D.Sc., F.R.S.

Advance copies of the Paper may be obtained from the Secretary, The Institution of Petroleum Technologists.

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. W. L. Bouch is home from Venezuela.
Mr. N. W. Grey has returned to Peru.
Mr. H. W. Lane has left for Persia.
Mr. G. H. May is home from Rumania.
Mr. H. M. Sale has returned to Assam.
Mr. D. Steel is now in Venezuela.

The Secretary would be glad to learn of the addresses of the following members: J. M. Brown, A. F. H. Gee, M. Jawad Jafar, J. Cecil Jones, E. L. Leites, P. B. M. Linton, A. MacLean, B. F. N. Macrorie, W. J. Reynolds, W. McKecknie Robson, and J. Towers.

Arthur W. Eastlake,
Honorary Secretary.

OBITUARY.

LORD GREENWAY OF STANBRIDGE EARLS.

It is with profound regret that we have to record the death, in his seventy-eighth year, of Lord Greenway, which occurred at his home at Stanbridge Earls, Hampshire, on 17th December, 1934, after a very brief illness.

Lord Greenway was a Founder Member of the Institution, and occupied the Presidential Chair from 1917 to 1919. He always took a keen interest in its affairs.

Born at Taunton in 1857, the son of the late Mr. John David Greenway, Mr. Charles Greenway (as he then was) went to India in 1885, and shortly after entered the employment of Messrs. Shaw, Wallace & Company. In due course he became a partner in the firm, and it was through their appointment as agents to the Burmah Oil Company that he came into contact with Persian Oil.

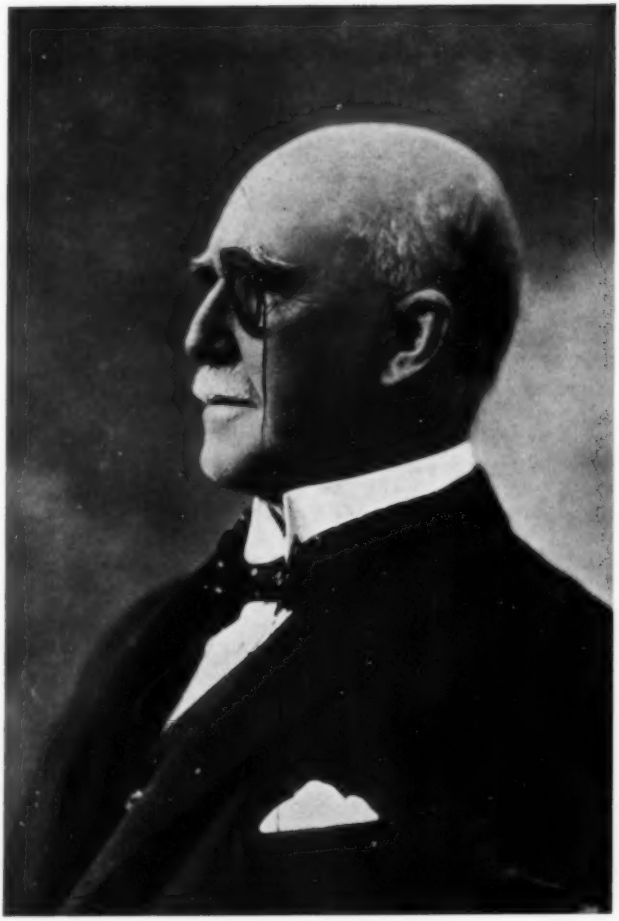
In 1908 he returned to England to devote all his time to the development of the Anglo-Persian Oil Company, of which he became Managing Director. On the death of the Chairman, Lord Strathcona, in 1914, he combined the duties of Chairman and Managing Director of the Company, and was responsible for the negotiations which led to the British Government taking an interest in the Company.

During the war and the immediate post-war period he personally directed the many activities of the Company, and for his services during the war a baronetcy was conferred upon him in 1919.

During the latter years of his Chairmanship he was assisted by a Management Committee, but still maintained active control of the Company's affairs until his retirement from executive office in 1927. He was then invited to become the Company's first President, a position which he filled until his death.

His services to the nation were publicly recognised by his elevation to the Peerage in 1927.

To Lady Greenway and her family we offer our sincere condolences.



THE LATE LORD GREENWAY.

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UNIV. OF MICH.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.
TRINIDAD BRANCH.

Fourth Annual Dinner.

THE Fourth Annual Dinner of the Trinidad Branch of the Institution was held on 27th October, 1934, the Chair being taken by Mr. G. H. Scott. More than 100 members and guests were present, the principal guest being His Excellency the Governor, Sir Claud Hollis, G.C.M.G., C.B.E.

The Hon. Sir Selwyn Grier, C.M.G., in proposing the toast of "The Institution of Petroleum Technologists," said that, as a result of the five years he had spent in the Colony, he was able to pay a definite tribute to the men in charge of the oil industry there, and to the co-operation and friendly relations existing between them and the Government.

He cited a recent case when the Government required data regarding soil values. The oil companies at once placed all the available information at their disposal.

In dealing with the budget, one realised how much the oil industry meant to Trinidad and how much it oiled the wheels of the financial machine.

He recalled a former suggestion of the Governor, and suggested that, in the interests of all concerned, there should be the closest co-operation between the different companies in regard to the marketing of their products.

Mr. G. H. Scott, in reply, said that mechanisation and scientific development had been largely blamed for the unemployment and over-production of recent years. It was a moot point whether the major blame should not be attached to the failure of the monetary and economic system of the world to adapt itself to changed conditions.

The scientific societies served as a valuable link between theory and practice, and encouraged the interchange of ideas, the value of which could not be over-estimated.

It was with regret that he announced the retirement from the Branch Committee of Mr. A. Frank Dabell, whose enthusiasm and initiative were responsible not only for the inauguration of the Branch, but largely also for its subsequent growth.

Commdr. H. V. Lavington, R.N., in proposing the toast of "The Industries of Trinidad," said that during the last three years there had been a definite improvement in industrial conditions throughout the world. People of different countries would no doubt attribute this improvement to widely different causes. A resident in the British Empire might say it was due to Imperial Preference.

In this connection he wished to express the gratitude of the oil industry in Trinidad to the Government and to those individuals who had assisted them in their claim for a preference for Empire Oil. It was to be hoped that before long the justice of the claim would be recognised.

Mr. John Pendrich (President, Chamber of Commerce), in reply, expressed the wish that the economic conditions of the major agricultural

industries of the island were such as to permit of his extolling their praises in the way he would like. During the last two years adverse weather conditions had affected production, and from the economic point of view the immediate future did not appear to offer any hope of a better outlook.

As regards asphalt and petroleum he could speak in a more cheerful spirit. The exports of petroleum in the present year had exceeded any previous year, resulting in further renown to the Colony as an oil-producing centre.

Mr. J. L. Harris proposed the toast of "Our Guest," and the Hon. F. Gordon-Smith (Attorney General) replied.

CONTENTS OF FEBRUARY JOURNAL.

The following Papers will be included in the February issue of the *Journal*:

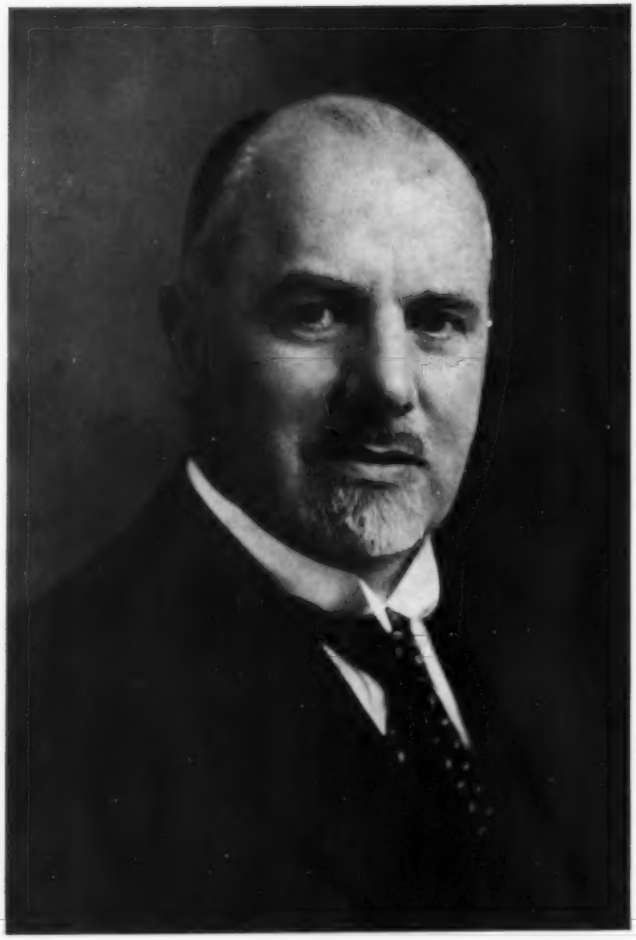
"Oil-Field Water Analysis. Part IV. Estimation of Sodium by Zinc Uranyl Acetate." W. R. Wiggins and C. E. Wood.

"Determination of Plate Efficiency in Fractionating Columns for Complex Mixtures." A. J. V. Underwood.

"Absorption." A. Newton.

"A Further Nomographic Study of Oil Pipe-line Design." L. V. W. Clark, R. Fallah, and A. W. Nash.

"Barytes Recovery from Muds." G. H. Scott.



T. Dewhurst, A.R.C.Sc., F.G.S.
President, 1933–1935.

[*To face p.* 1.

UNIV OF MICH

THE UTILISATION OF PARAFFIN WAX AND PETROLEUM CERESIN.*

By P. G. Higgs, B.A. (Associate Member).

SYNOPSIS.

A short historical introduction is followed by an account of the modern uses of petroleum waxes. Special attention is given to the waterproofing of paper, polish-making, and electrical uses.

Certain properties which are relevant to utilisation are discussed and paraffin wax emulsions are also dealt with.

Petroleum ceresins are described generally and their use as a dope for paraffin wax is suggested.

A FEATURE of chemical industry at the beginning of the nineteenth century was the recognition of the value of dry distillation when applied to complex organic materials. The early gas industry stimulated its free extension to a large variety of substances other than coal, chiefly with the object of obtaining volatile solvents to supplement the supplies of coal-tar naphtha. In the light of present knowledge it would seem inevitable that the choice of a suitable raw material would lead, sooner or later, to the production of paraffin wax.

The discovery was, in fact, announced twice within the space of a few months by two men, Carl von Reichenbach, a Moravian industrial chemist, and Dr. Robt. Christison, of Edinburgh University, each of whom was unaware of the other's activities. Reichenbach reported in 1830 [1] that he had obtained the material by dry distilling wood-tars, and the completeness of his description, as well as his actual priority, entitles him to be regarded as the true discoverer; to him, incidentally, the name *paraffine* was due.

Christison [2] separated paraffin wax from the distillation products of Burmese petroleum, and is remembered as the first to prepare and identify the wax from crude petroleum oil, the principal source to-day.

During the period 1830–50 numerous schemes were evolved in France and England for processing bituminous shales on a large scale, but their success was short-lived and is difficult to estimate. Peat was also used as a raw material in Ireland and elsewhere. Work of this type came to fruition in the achievements of James Young, who at last placed the manufacture of paraffin wax on a commercial footing.

In the middle fifties a small but regular production of paraffin wax was being obtained from Burmese petroleum, imported and refined in this country; it is on record,[3] in fact, that in 1857, 25 tons of paraffin wax candles from this source were made by Price's Patent Candle Co., but the real economic history of the wax began only after the Scotch shale industry, founded on Young's work, had been well established. At about the same time, American petroleum was discovered, and wax from this

* Paper presented for discussion at the One Hundred and Sixty-first Meeting of the Institution of Petroleum Technologists, December 11th, 1934.

source became so plentiful that, according to Ure's Dictionary of 1878, in 1866 there was more than enough to satisfy the demands of the time. The subsequent development of the petroleum industry in other parts of the world, particularly in Burma, the East Indies, and Persia, not only further augmented the supply of paraffin wax, but also widened its scope by extending the range of grades. The large choice of melting-points which is afforded by present-day commercial waxes has resulted from the working of new crudes and the gradual improvement of wax-refining technique; to the latter much has been contributed by the Scotch shale industry and by the English candle trade. With the regular production of Eastern high melting-point grades, which began about thirty years ago, the usefulness of paraffin wax was greatly increased.

The so-called petroleum ceresins, though totally different in character from the ordinary paraffin waxes, are the most recent addition to the waxes which can be offered by the petroleum industry. Until the end of the nineteenth century the only property of paraffin wax which had an important market value was its combustibility; its other well-known characteristics—resistance to water, inertness, good electrical properties, etc.—were recognised but had been applied only occasionally. Within the last thirty years or so numerous uses for the wax have been brought into prominence by progress in other fields. To-day, food-stuffs, etc. are received by the retailer in small packages, ready for sale, rather than in bulk; the modern practice has set up new standards for the packing material itself which have been met effectively by waxed paper. The expansion of telegraph and radio communications has led to a large demand for paraffin wax for insulation purposes; certain of the long-established applications, *e.g.* polish-making, are now carried out on a much larger scale; and the minor uses, representing collectively a large off-take of wax, increase in number almost daily.

The Applications of Paraffin Wax.

The ease with which paraffin wax may be adapted to very varied operating conditions is responsible in great measure for the diversity of its uses. It melts readily at a low temperature and may be kept liquid by simple means; on melting, it immediately yields a liquid of very low viscosity and is, therefore, well suited to impregnation work requiring high fluidity without the necessity for high temperature.

Paraffin wax is marketed in convenient forms which lend themselves to ease of handling—the lower-melting grades in casks, and the higher-melting refined grades in cakes of a manageable size. In the United States refined wax is frequently transported in the melted condition by insulated rail-cars when it is required for immediate service.

In the majority of cases the wax is used simply after melting. In this form it is applied by vacuum impregnation, bath impregnation, roller waxing, and, to an increasing extent, by spraying. Less direct methods for its utilisation are by means of solutions or emulsions.

The following account must of necessity be restricted to the more important applications of paraffin wax, the minor uses being exemplified by passing reference and demonstration.

Paraffin Wax as an Illuminant.—The candle industry is still the largest consumer of paraffin wax, but since the Institution has already heard an authoritative account of this,[4] there is little that the author is qualified to add. The economic importance of the wax to candle-making requires no stressing; its technical value lies in its good appearance, its satisfactory burning properties (freedom from mineral matter, high illuminating power, etc.), and the facility with which it may be moulded. It has disadvantages—*e.g.* its tendency to bend and liability to mottle—but the candle-maker is able to cope with them successfully.

The tendency to bend, or any other property which is closely connected with composition, cannot be judged from the setting-point of the wax. Various suggestions have been made to combine with the setting-point determination some other test which is more sensitive to the lower melting constituents of the wax, with the idea of estimating the width of cut. Dawidson and Pilat [5] have claimed, for instance, that this purpose is served by the difference between the cooling-curve setting-point (Shukoff method) and the Ring and Ball melting-point. It has been found that this procedure will differentiate between extreme cases but shows very little difference between most ordinary commercial waxes. A slightly better distinction may be made if the Shukoff setting-point be replaced by the temperature at which turbidity is first produced when the melted wax is slowly cooled. In either case, however, the results do not necessarily place waxes in the order of their plastic properties or bending tendency, which are undoubtedly influenced by such factors as crystallinity and oil-content, as well as by width of cut.

Paraffin wax of very low setting-point (about 100° F.) has been used since the earliest days as an illuminant by burning in specially constructed wick-lamps. These are still employed for lighting ships' holds and warehouses, and by miners working in surface mines.

The use of the lower grades of paraffin wax (setting-point 106–115° F.) in the match industry may conveniently be noticed here. Every match splint is treated with wax before the head is put on, in order to facilitate the ignition of the wood; for a second or two after striking, before the wood itself is well alight, the splint, saturated with wax, functions similarly to a candle. Match splints of square section are dipped in wax to a depth of about $\frac{3}{16}$ in. only, but the round variety need to be completely immersed, since the absence of corners causes them to ignite a little less easily. Match wax is required to have good impregnating qualities and must not so affect the striking composition, which is applied immediately after waxing, as to prolong its drying time or lessen its adhesion to the splint. It is doubtful whether a large oil-content adversely affects these properties; wax-oil blends containing up to 50 per cent. oil have been stated to be satisfactory, provided that the viscosity of the oil be correctly chosen.[6]

Paraffin Wax as a Proofing Agent.—This heading covers those applications in which porous materials such as paper, fabrics, wood, and leather are made impermeable to air, water, or water-vapour.

Proofing against liquid water may be accomplished either by filling up the interstices of the material or by treating the fibres with sufficient wax to make them water-repellent; proofing against air or water-vapour, however, is possible only by the first alternative.

The interest attaching to this subject and its growing importance, particularly in the case of the paper treatment, make a fairly detailed account desirable.

Waxed Paper and Paper-Board.—Many specially prepared papers have been designed to be waterproof, but of these, waxed paper has proved the cheapest and easiest to make; its efficiency is of a high order and will be referred to again.

The value of refined paraffin wax for paper treatment lies in its insolubility, stability, and innocuousness. There can be no doubt as to its lack of physiological activity, though it is not itself antiseptic. The low temperature at which it can be applied ensures that the mechanical properties of the paper suffer but little damage as a result of loss of natural moisture.

There are two main methods of waxing paper and paper-board:

(*a*) By the application of a surface coating.

(*b*) By impregnation.

The method to be adopted in a particular case depends on the article which is being manufactured. Cartons and boxes which are not intended to contain actual liquids are made up from flat blanks, previously surface-waxed. Containers for liquids—*e.g.* milk cartons—and those of such a shape that assembly from previously waxed paper or board would present difficulties, must be impregnated after manufacture. Until recently it was not possible to surface-wax three-dimensional articles of the latter type, but the recent introduction of wax-spraying processes promises to make this practicable.

Packages which have subsequently to be stored at low temperatures, and which would otherwise be merely surface-waxed, should be impregnated in order to prevent the removal of the protecting effect of the wax by cracking and flaking.

(a) *Surface-Waxing.*—The usual type of waxing machine for paper or board in flat form consists essentially of a number of horizontal rollers; the lowest of these rotates in a bath of molten wax and transfers wax to one or more of the others, between which the paper is passed. If the paper travels at a high speed, and especially if the temperature of the rollers is not too high, the film of wax solidifies before it can penetrate far into the body of the paper. Complete impregnation can be effected, if required, by passing the surface-waxed paper through a further pair of heated rollers.

This method of waxing is very rapid; no drainage period is necessary, since there is no excess of wax on the paper, and the hardening period is very short. On the other hand, paper treated in this way lacks the extra sturdiness and support which are obtained by thorough impregnation with wax.

Waxed paper-board of this type is used for making a large variety of containers—cake boxes, lard cartons, etc.—which must prevent the passage of grease or moisture from their contents. The blanks are stamped out and printed before waxing.

The extent of the wax penetration in a surface-waxing process may be varied fairly widely by adjusting the temperature of the rollers and time of contact of the paper with the waxing rollers.

There is some demand for wrappings waxed on one side only, and such paper may be made in a machine of the above type by a suitable arrangement of the rollers. Single coating was suggested by Frensel [7] as long ago as 1904, when any waxed paper was a great speciality, but the object was simply to reduce the greasiness which was associated with the products obtainable at the time.

(b) *Impregnation.*—Highly-proofed wrapping papers and shaped articles, such as paper milk cartons, are treated by actual immersion in molten paraffin wax under conditions which favour more or less complete impregnation.

Wrapping paper for bread covers, biscuit packings, external box wrappers, etc. is passed from a large reel, under a guide roll immersed in wax, and then, on emerging from the bath, through a roller or other device to remove excess wax. The waxed strip is next cooled by an air-blast or by contact with a water-cooled drum, and is finally re-reeled.

A shaped article is carried through the wax by an endless conveyor and is kept completely immersed for a few seconds. It is held in such a position that all air bubbles in its interior may rise to the surface of the wax. On leaving the bath, the conveyor carries the article until draining and hardening of the wax have been accomplished. The duration of the process varies considerably from one case to another, but the waxing and cooling are usually completed in a few minutes.

Impregnation treatment is, of course, much less economical of wax than is surface-waxing, the actual consumption depending on the completeness of drainage and on the porosity of the paper.

The choice of paper for surface-waxing is not important, but requires care when impregnation is in view; in the latter case the presence of unbleached material causes darkening to occur. Cartons are frequently made from board consisting of dark layers surfaced with white paper of good quality; these may be surface-waxed but cannot be impregnated without suffering in appearance.

In general, it is necessary for impregnation purposes to use a uniform paper or board made from a well-bleached pulp and containing a minimum of size. Highly beaten papers are selected for the manufacture of exceptionally transparent waxed wrappings, while the presence of fillers such as barium sulphate and titanium oxide is necessary when the paper is required to remain opaque after waxing.

Several arbitrary methods have been proposed for comparing the efficiency of wrapping materials with respect to their permeability to water vapour.[8] In all cases the weight of water is determined which passes as vapour through a standard area of the material in a given time under the influence of a fixed difference in humidity between the two sides. When compared with other common wrappings, impregnated waxed paper is found by all methods to be the most efficient; even after severe creasing its efficiency is still of a high order but is appreciably lessened by imperfections in the paper itself. Surface-waxed paper or board is much more permeable to air and water-vapour, though it resists the passage of liquid water.

Paraffin wax for the treatment of paper is required to be fully refined and without odour or taste. The critical attitude taken by the paper

trade on the question of odour has made it more necessary than ever to control carefully factors such as efficiency of fractionation in the production of wax-distillate, oil removal, and the final chemical treatment of the wax. Paraffin wax readily acquires odours from external sources and has, in fact, been used as an extractive in perfumery [9]; if it is intended for paper treatment, it should therefore be stored and despatched so that it is not in direct contact with odorous packing materials such as certain fabrics and woods. On the user's side, it is equally important to minimise the development of odour during service, due to mild oxidation, by careful temperature control.

At temperatures up to 100° C. paraffin wax is practically inert towards air or oxygen, but as the temperature is raised above 100° C. the rate of attack becomes increasingly greater.

It frequently happens that the wax in impregnating baths, etc. is heated in air for long periods at a time at temperatures little below that at which oxidation begins to take place at a measurable rate. In such cases temperature control should obviously be a first consideration.

The products of mild oxidation are complex, but their effect on the general quality of the wax is to confer acidity, odour, and colour. Though very little oxidised material is formed as a rule it is sufficient to make the wax unfit for many purposes.

The safest method of heating wax-impregnating baths is by means of coils circulating steam at about 100° C. Gas and electrically heated baths are in use, but they are not easily controlled thermostatically and so entail a risk of overheating.

Miscellaneous Proofing Processes.—The use of paraffin wax as a proofing agent is by no means restricted to the treatment of paper. Many kinds of wooden packages—*e.g.* butter kiers and beer barrels—are commonly brushed or sprayed internally with wax in order to prevent tainting of the contents by the wood and loss in weight during storage. Roofing shingles and other wooden articles to be exposed outdoors are frequently waxed by impregnation. In this connection it has been found [10] that more thorough penetration occurs if the wood is first soaked in water for 12 hours and then impregnated with wax at above 100° C.

The wax is also used in the manufacture of chrome-tanned leather and in admixture with fats for waterproofing and fulling sole-leather and belting; it has been applied to some extent to the preservation of urban stone-work, but opinion is divided as to the effectiveness of such processes, though there seem to be several well-authenticated cases in which success has been achieved.

Certain food-stuffs which must maintain their quality during export or prolonged storage may be waxed directly. In the Californian fruit-packing industry citrus fruits are coated with a very thin film either by rubbing between blocks of paraffin wax or more frequently nowadays by spraying with wax followed by brush polishing. This treatment greatly retards shrinkage and inhibits mould formation.

Certain kinds of Continental and Colonial cheeses and the small varieties which cannot be bandaged in the ordinary way are coated by dipping in the molten wax in order to prevent loss in weight and to retain the moisture necessary for their proper ripening.

The Manufacture of Polishes.—The consumption of paraffin wax in polish manufacture is very large and is next in importance to that of the paper trade, the bulk of it entering into the preparation of paste polishes for furniture and leather. These consist usually of a mixture of waxes together with a solvent, such as turpentine or white spirit, which is insufficient in quantity to dissolve more than a small proportion of the total wax at ordinary temperatures. Paraffin wax itself has poor polishing qualities, but its purpose is to secure the required pastiness without the use of unnecessarily large proportions of expensive waxes of animal or vegetable origin. All grades are sold for polish-making, but for the best quality products the higher melting-points (130° F. upwards) are preferred and probably result in better stability in warm weather.

An important function of the wax in paste polishes is to prevent too rapid evaporation of the solvent and so to increase the spreading capacity. Ivanovszky [11] has stated that paraffin wax shows poor solvent retention, but he expressed no view as to the reason for this behaviour. The crystallinity of paraffin wax on separating from solution is probably partly responsible. It is unlikely, however, that the low solvent retention of the wax is sufficiently serious from a practical view-point to outweigh the advantages of its cheapness and its structural effect in polishes.

Applications in Electrical Industries.—Large quantities of paraffin wax are used in admixture with other materials in compounds for sealing dry batteries, etc. and for filling cable junction and terminal boxes. It is used alone as a filling for instrument transformers and as an impregnant for the insulation of inductance coils, windings, and cables of all sizes.

In many cases paraffin wax is used simply for waterproofing other forms of insulation. The only extensive use of the wax, unmixed with other ingredients, in which its electrical properties are comparable in importance with water resistance is in the construction of paper/metal fixed condensers. The latter, which have been used for many years in telegraphy and on a large scale in the wireless trade, are generally made by the method introduced by Mansbridge.[12] Continuous strips of paper and aluminium, which constitute the dielectric and plates respectively, are wound together until the required capacity has been built up. The whole condenser is then dried and treated with paraffin wax, vacuum impregnation being necessary in order to secure thorough penetration of the paper. In this type of condenser the electrical properties of the waxed paper dielectric, hence of the wax itself, are of great importance; in particular, the insulation resistance, absorption, and break-down voltage must be adequate to the working conditions of the instrument. Paraffin wax is considered satisfactory with respect to these properties, but to ensure their constancy the absorption of water-vapour into the inter-crystal spaces of the wax must be minimised as far as possible. This water absorption is, of course, extremely small and is only shown up by the great sensitivity of electrical tests; it is in no way opposed to the use of the wax as a proofing agent in the more general sense. In the manufacture of condensers the usual precautions are to avoid unnecessary handling and to seal the waxed instruments as quickly as possible after impregnation.

Lee and Lowry [13] have shown with regard to the absorption of liquid

water, as judged from electrical measurements, that paraffin wax is, in fact, superior to most other common dielectric materials.

Paraffin wax of high setting-point is usually selected for electrical purposes in view of the high working temperatures which it must frequently meet without melting out of the apparatus. The electrical properties of wax vary rapidly and somewhat irregularly with rising temperature as the melting-point is approached. This behaviour is undesirable in certain instruments in which invariability is important, such as condensers for radio-frequency circuits. If high setting-point wax is used, its average working temperature will probably be well below that at which extreme changes in resistance and dielectric properties begin to occur. As in the waxing of paper, mild oxidation of the wax by overheating must be minimised as far as possible by adequate temperature control. The formation of acidic oxidation products, potentially corrosive to copper, and water is particularly undesirable in wax for electrical purposes. In practice, the rate of oxidation is lessened by the usual adoption of vacuum impregnation not only for condensers but also for coils, cables, etc. At certain stages of the process, however, the heated wax is in contact with air, and so may oxidise; since the wax is usually re-cycled many times the effect of very slight oxidation is cumulative.

A series of simple heat tests has shown that both the development of acidity and the rate of corrosion of copper, judged by the formation of green colour, are greatly accelerated by high wax temperatures.

Equal weights of a refined wax (135/140° F. grade) were heated at a number of temperatures (100–170° C.) with very gentle stirring, in small glass beakers. The latter were of equal dimensions and open to the air. In all the tests but one a strip of clean copper gauze was immersed in the melted wax. In all cases the heating was continued until each sample had approximately the same acid value. The test at 120° C. was prolonged beyond this stage in order to observe when corrosion of the copper became evident. The observations made in this experiment are given in Table 1.

TABLE 1.

Heat Tests on Refined 135/140 Paraffin Wax in the Presence of Copper.

Temperature.	Time of heating.	Acid value (equiv. mgm. KOH/1 grm.).	Appearance, etc.
100° C.	20 hours	nil	Colourless; extremely slight odour.
120° C.	9 hours	0·25	Colourless; distinct "coconut-oil" odour.
	18 hours	0·44	Very pale green; distinct odour.
150° C.	2½ hours	0·03	Pale green.
	5 hours	0·20	Bright green; strong odour.
170° C.	1 hour	0·21	Bright green; strong odour.
	1 hour (in absence of copper).	0·28	Very slightly yellow; strong odour.

It will be noted that acid value in itself gives no indication of the potential corrosive action of the wax on copper instruments during impregnation. After 18 hours at 120° C. the acid value was the highest (0·44) observed

in the tests, but the metal was scarcely attacked; this sample became bright green when further heated at 150° C. with copper for a few minutes. At 150° C. and 170° C. much lower acid values caused rapid corrosion. It appears that the temperature of the wax may be high enough to cause the fairly rapid formation of organic acids but may be below that at which the acids readily attack copper.

Incidentally the above tests bear out the general experience that when the formation of odour is undesirable, *e.g.* in the treatment of paper, the maximum temperature for open impregnating baths should not be much above 100° C., particularly when the wax consumption is slow.

Indirect Methods of Applying Paraffin Wax.—For certain purposes paraffin wax is conveniently used in solution or emulsion instead of by direct application after melting.

In emulsion or dilute solution the wax may be applied at ordinary temperatures; a very light waxing treatment may be given in this way, *e.g.* in the waterproofing of fabrics and in the dressing of shoe upper leather.

Saturated solutions, excess wax being present, as in certain polishes and paint strippers, enable the wax to be used in paste form.

The *solubility relationships* of paraffin wax at air temperatures are, therefore, of practical interest.

Among the best solvents are chlorinated hydrocarbons and liquid hydrocarbons themselves, the latter including benzol, turpentine, and the lighter petroleum fractions. As a general rule, oxygenated liquids are poor solvents for wax. At 15° C., even in the most favourable media, the solubility of refined commercial waxes is relatively low, but it increases rapidly with rise in temperature. It is impossible to quote hard-and-fast solubility data, since, for any one solvent, the figures vary with the width of cut, the source, and the setting-point of the wax. Moreover, the measurement of solubility by the usual method has been found to present difficulties; results have varied, even in the same sample, with the time of contact between solid and liquid and with the actual excess of wax taken for saturation.

For many practical purposes the saturation point is deemed to have been reached when a clear, dilute solution of paraffin wax becomes just turbid on cooling. On this basis the solubility curves of a wax in the more favourable solvents may be determined by finding the temperatures at which solutions of known concentration become uniformly cloudy when cooled very slowly. The clearing-point on warming the cloudy liquid is more difficult to observe, but it can usually be obtained to within 1° C. of the temperature of initial turbidity. The approximate solubility data given in Table 2 for a number of commercial samples were derived by this method and are merely illustrative.

The figures in Table 2 are influenced mainly by the higher melting, less soluble constituents of the waxes, and their chief value is that they have a practical interpretation; each figure represents the maximum concentration of wax which can be used in order to ensure a clear solution at the temperature concerned. In the case of the higher setting-point waxes it has been found that the results up to 25° C. are not very different from the true solubility, that is, the total material dissolved after prolonged contact of the solvent with excess wax at a given temperature. The

results given in Table 3 for benzene solutions illustrate the general order of agreement between the two methods.

TABLE 2.

Approximate Solubilities as given by Initial Turbidity Temperatures.
(Parts wt. in 100 parts wt. solution.)

Wax.	Benzene.		Carbon tetrachloride.	
	At 15° C.	At 25° C.	At 15° C.	At 25° C.
Borneo, S.P. 137° F. .	2	10	5	13
Persian, S.P. 134° F. .	4	16	6	16
Polish, S.P. 125° F. . .	5	22	8	24
Scotch, S.P. 118° F. . .	9	30	11	27
	High aromatic white spirit.		Genuine American turpentine.	
	At 15° C.	At 25° C.	At 15° C.	At 25° C.
Borneo, S.P. 137° F. .	2	14	3	12
Persian, S.P. 134° F. .	5	17	4	16
Polish, S.P. 125° F. . .	9	22	9	20
Scotch, S.P. 118° F. . .	13	25	12	27

TABLE 3.

Solubility in Benzene at 25° C.
(Parts wt. in 100 parts wt. solution.)

Wax.	Initial turbidity temperature.	True Solubility.*
Borneo, S.P. 137° F. . .	10	11·4
Rangoon, S.P. 136° F. . .	12·5	13·5
Persian, S.P. 134° F. . .	16	17·3
Borneo, S.P. 128° F. . .	23	24·6
Polish, S.P. 125° F. . .	22	28·4
Scotch, S.P. 118° F. . .	30	33·5

* CONDITIONS OF TEST.

Time of contact	6 hours
Excess of wax	20% on I.T.T. value
Condition of sample	Finely ground

Paraffin Wax Emulsions.—A demand for aqueous emulsions has arisen chiefly in connection with the replacement of more expensive materials—Japan wax, montan, or beeswax—which emulsify fairly readily. As examples may be quoted the use of paraffin wax emulsions in the sizing of paper, as a size in the weaving of cotton, and in the laundry trade as a glossing agent in the calendering of linen.

The utilisation of paraffin wax in emulsion form should be capable of considerable extension and is worth more attention than it receives at present.

In the preparation of a paraffin wax/water emulsion it is always neces-

sary to add an emulsifying agent, the requisite amount (relative to wax) and the nature of which depend largely on the method of emulsification.

Stable emulsions may be made containing emulsifying agent in the low ratio 1 : 20 on the total wax, but an especially efficient dispersing mechanism of slow output is required. The following is an example of a concentrated emulsion of this type, easily prepared in a Hurrell mill:

Paraffin wax	33·3% (wt.)
Potassium oleate	1·8% ,,
Potassium hydroxide	0·1% ,,
Soft water	64·8% ,,

When more dilute emulsions are required it is best first to make a concentrate such as the above, which can then be diluted. In practice, a more economical rate of manufacture is generally necessary, and in the commoner types of equipment a larger proportion of emulsifying agent must be added to compensate for less thorough dispersion. When adequate dispersion has once been secured the ordinary emulsifying agents in general use seem quite effective in small proportions.

It is frequently desired to make paraffin wax emulsions without the aid of mechanical dispersion. The choice of emulsifying agent is then more critical; soaps are most commonly used, those of triethanolamine being the most effective. Ammonium soaps are also very satisfactory and are superior to the corresponding sodium or potassium compounds. In all cases the soap should be made *in situ*. The stability of the emulsions is not so high as when mechanical dispersion is used, but slow "creaming" is not usually regarded as serious provided that the separation does not take the form of solid lumps.

The following emulsion is illustrative of those which can be made by simple mixing:

Paraffin wax	33% (wt.)	or	33 lb.
Oleic acid	3% ,,		3 lb.
0·880 Ammonia solution	0·6% ,,		0·55 pint
Soft water	63·4% ,,		6·4 gallons

The water is warmed to about 160° F. and the ammonia solution added. The wax and oleic acid, previously melted together, are poured into the water phase, the mixture being well stirred or shaken.

Petroleum Ceresins.

It has long been known that a type of solid hydrocarbon occurs in petroleum which cannot be classed with distillate paraffin wax. Such material is frequently deposited spontaneously from crude oil in wells, pipe-lines, etc.; it is only within recent years, however, that deliberate efforts have been made to isolate it from crude oil for its own sake. The manufactured substance may conveniently be termed petroleum ceresin, although, as with ozokerite ceresin, its true nature is little understood. The ceresin from crude oil may differ physically in several respects from that obtained by refining ozokerite, but there is a strong possibility that both are basically of a similar constitution.

Petroleum ceresins are characterised by relatively high setting-point

and microcrystalline structure. They are usually non-distillates, the general method of isolation being by the dilution of a suitable waxy residue by means of a volatile solvent for oil. After settling at a suitable temperature the precipitated ceresin is recovered by filtration or centrifuging and is subsequently refined. The details of the process are important and form the subject of many patents.

Sachanov and his collaborators [14] have described ceresins recoverable from certain Russian crudes and have stated that when compared with distillate wax of the same setting-point they are found to have higher molecular weight, viscosity, and boiling-point. The results of X-ray crystal analyses have suggested that series other than straight chain paraffins are present in petroleum waxes, ordinary distillate wax having been stated to contain not only branched chain members,[15] but also cyclic compounds.[16, 17] The constitution of the relatively less volatile series, concentrated in a petroleum ceresin, is even more uncertain.

Whatever their true nature may be, petroleum ceresins have become commercial products and have proved a valuable addition to the range of petroleum waxes now available to industry. Since a considerable variation in physical properties is shown according to the source and mode of manufacture, the following account will be restricted mainly to a substance with which the author is best acquainted.

The petroleum ceresins as a class melt at relatively high temperatures. Those obtainable from certain East Indian crudes are especially noteworthy in this respect and have been made with setting-points as high as 93° C. The best known from this source is a hard material setting at about 85° C. and possessing a granular, microcrystalline structure; as marketed at present it is orange-yellow, the further reduction in colour presenting difficulty. It has been used with success as a substitute for certain of the high-melting natural waxes, such as carnauba, insect, and beeswax, and has an advantage in containing no acidic constituents. The latter characteristic in conjunction with its microcrystalline structure has led to its use for impregnating electrical instruments and particularly as a "potting" material for small transformers. The low solubility of this ceresin in the usual solvents, even at high summer temperatures, makes it especially suitable for inclusion in paste polishes which are required to retain their consistency over a wide temperature range. In general, it is of value in many cases when a high setting-point is required provided that the question of colour is of no consequence.

Petroleum Ceresin as a Dope for Paraffin Wax.—Perhaps the most interesting property of petroleum ceresins is their effect on the crystallinity of ordinary distillate paraffin waxes. It has been known for many years that certain mixtures of ozokerite ceresin with paraffin waxes are of a minutely crystalline nature. Petroleum ceresins, however, show a much greater activity in this respect. This property has been remarked in a general way by several observers, but the exceptional activity of these ceresins does not appear to have been fully appreciated.

In the case of the East Indian ceresin described above it has been found that the addition of 0·3 per cent. (and occasionally less) is sufficient to render commercial paraffin wax almost microcrystalline. All the characteristics of the original wax which are due, directly or otherwise, to

marked crystallinity are then much modified; a high-melting wax which is normally highly crystalline and crumbly assumes a compact, granular structure and shows no sign of its original fragility; mottling and mealiness in a wax which has been insufficiently de-oiled are much reduced and do not appear at all unless the oil-content is exceptionally active.

It has been found repeatedly that candles made from paraffin wax to which 0·2–0·3 per cent. petroleum ceresin has been added display increased resistance to bending. The relative improvement is not the same for all waxes of different origin and similar setting-point, but the effect is in all cases quite definite. It is not likely that so small an addition of the ceresin would have a stiffening action of the type shown by stearine or even by larger proportions of the same ceresin, but rather that the plastic properties of the wax are influenced, in part at least, by the crystal size and the consequent degree of compactness. In this connection it has been established that a definite modification of the Dow ductility curve is caused by the addition of a small amount (0·5 per cent. in this case) of petroleum ceresin to some of the Eastern waxes. The maximum ductility is decreased and is reached at a lower temperature, while the temperature range over which any ductility at all is shown by the wax is narrowed.

In studying the comparative bending tendencies of paraffin wax, both unmixed and with the addition of the ceresin, care was taken to ensure that the candles were made under the same conditions. Two identical moulds were surrounded by a water-jacket, through which cooling water was circulated at about 70° F. below the setting-point of the waxes (the addition of 0·3 per cent. petroleum ceresin does not affect the setting-point), and the moulding temperature of the waxes was the same in each instance. After moulding, the candles were allowed to remain at room temperature for not less than 18 hours. Comparative bending tests were made by clamping the candles horizontally in an oven controlled thermostatically at a suitable temperature (usually 90–95° F.). After a time, which varied from 1 to 6 hours according to the setting-point of the wax, sufficient bending had occurred in both candles to enable a visual comparison to be made.

The efficiency of petroleum ceresin in reducing the crystal size of paraffin wax is well shown by allowing a fairly concentrated solution (say 20 per cent. wt.) in a suitable solvent to cool to ordinary temperature from a higher at which the solution is clear. Solutions of ordinary paraffin wax deposit large crystals which gradually increase in quantity until the whole mixture becomes a porous mass of large, interlacing crystals amongst which the solvent is entrained. If this mass is allowed to warm up slowly, gradual dissolution occurs and the loose crystals settle, leaving above them an increasing layer of clear liquid. On the other hand, if the solution is prepared from paraffin wax containing 0·3 per cent. petroleum ceresin, a smooth, cream-like mass composed of very small crystals distributed evenly throughout the solvent is obtained on cooling. In some cases, in fact, the cold mixture has been found almost gelatinous. On slowly warming, the paraffin wax re-dissolves as in the first instance, but the residue at any moment remains evenly distributed and does not settle. The separation of clear liquid is delayed until practically all the wax has returned into solution.

This behaviour is desirable in certain wax/solvent mixtures, such as paste polishes and paint strippers, and the possibility of using a small proportion of petroleum ceresin in their manufacture is worth consideration.

A disadvantage of most petroleum ceresins is their strong colour. Less than 0·5 per cent. of the ceresin concerned in the foregoing account confers a definite yellow tint on paraffin wax. Laboratory experiments have suggested, however, that the crude ceresin (0·3 per cent.) may be added during the manufacture of the paraffin wax, after sweating but before the final treatment (acid, earth and lime; earth or bauxite), the two materials being refined together. The product is of good colour and the effects of the ceresin on the structure are retained. Such wax is pleasing in appearance, being almost entirely free from the mottling and lack of uniformity shown by many pan-moulded commercial waxes, while the other defects consequent upon strong crystallinity are absent or much remedied.

It must be stated that the activity of petroleum ceresin with respect to its action on paraffin wax structure is greatest in the case of commercial waxes which initially have a pronounced tendency to crystallise strongly, *e.g.* Assam, Burmese, and East Indian waxes. The Polish waxes do not respond well and Persian grades for some unknown reason are somewhat less readily affected than are the Eastern waxes. So far as can be judged at present, there seems to be a reasonable prospect of increasing the usefulness of paraffin wax—for certain purposes at least—by a modification of its crystalline structure in the above manner. The advisability of manufacturing doped waxes, or, alternatively, of leaving such doping to the user, is admittedly a controversial question. Nevertheless, it is evident that the commercial grades at present available cannot be equally satisfactory for all the diverse modern applications of paraffin wax.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The One Hundred and Sixty-First General Meeting of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, London, W.C.2, on Tuesday, December 11th, 1934. The President, Mr. T. Dewhurst, occupied the Chair.

The following paper was presented :—

"THE UTILISATION OF PARAFFIN WAX AND PETROLEUM CERESIN." *

By Mr. P. G. Higgs, B.A. (Associate Member).

DISCUSSION.

The President said the Author had given a clear and straightforward account of the utilisation of paraffin wax and of petroleum ceresin. The modern uses of petroleum wax were manifold, and it was satisfactory that at least the minor uses of it were increasing in number almost daily. The Author had rightly given special attention to such important uses as the waterproofing of paper, polish-making, and insulation in the electrical industries. The comments made in the paper on the properties which bore on the utilisation of paraffin wax and paraffin-wax emulsions were also of considerable interest, and should give rise to some discussion. Petroleum ceresin administered as a dope extended the temperature range of solid paraffin and increased its sphere of usefulness.

To the layman, the paper, as an exposition of the title, appeared to be detailed and accurate, and so complete as to provide little room for discussion, but fortunately there were present at the meeting specialists who would view the paper much more critically, who would doubtless seek further elucidation of many points, and would indeed contribute important additional facts and also new and fruitful points of view.

Mr. J. S. Jackson said that very little information had been published regarding paraffin wax, and except for certain limited purposes, this product had been rather neglected. He felt that the possibility of using it by spraying and in the emulsified form must certainly open up new outlets.

He was most interested in the Author's experiments in connection with petroleum ceresin. The effect of this product on crystal formation in paraffin wax would probably be of special importance in connection with the use of paraffin wax in the electrical industries. It was well known that the readiness with which minute quantities of water penetrate paraffin-wax films gives rise to many problems in this connection. It appeared probable that the resistance of paraffin wax to water could be improved by the addition of petroleum ceresin. He thought that the experiment shown by the Author illustrating the way in which a relatively small proportion of petroleum ceresin stabilised a suspension, indicated a property which should

* See pp. 1–14.

be of interest to the manufacturers of polishes, paint removers, etc. He pointed out that while this petroleum ceresin was not ordinarily refined to a pure white colour, refining to a better colour would not present any serious difficulty.

He felt that paraffin-wax emulsions had been strangely neglected. He did not see why emulsified paraffin wax should not become a useful commercial product. Paraffin wax was easily dispersed mechanically; and it was merely a matter of choosing a suitable stabiliser to give the measure of stability required for any particular purpose.

With regard to the effect of heat on paraffin wax, he was glad that this point had been emphasised by the Author, and he would like to emphasise it still further. It always amazed him that technical men, who were quite familiar with the nature of paraffin wax, did not realise that it should not be heated to high temperatures day after day in thin films under oxidising conditions. The Author's experiments indicating that 120° C. must be regarded as a critical temperature were of special interest.

It was rather surprising that greater attention had not been given to the design of paraffin-wax baths, and that the importance of controlling the temperature accurately throughout the whole bath, and particularly in the neighbourhood of the heaters, had not been more generally appreciated.

He hoped that the paper would serve the important purpose of stimulating suggestions for further investigations and for further uses of paraffin wax.

Mr. C. R. Scott-Harley referred to the recent use of coloured wax paper for street decorations and its efficaciousness against the elements.

Although the Author had demonstrated a remarkable variety of comparatively new applications for wax, there was another which he thought might be of interest. Quite a number of manufacturers prefer to use heavily pigmented oil-base inks for printing, but these suffer from the disadvantage that they require from 24 to 48 hrs. to dry sufficiently to be packed. He discovered the rather surprising fact that it is quite possible to apply molten wax to a wet inked surface, and that it immediately acts as a protective film and enables the article to be handled without further delay. Such a system of combined printing and waxing is now being conducted with every satisfaction.

Another offshoot of the same principle is the spraying of a high-melting-point wax, not necessarily paraffin wax, on to lithographic prints immediately after leaving the printing-rolls. The wax is deposited in the form of an impalpably fine powder, and must possess a definite hardness to support a mass of paper about 4 feet high for 12–24 hrs. whilst the ink is drying before the particles collapse. As this wax cannot be detected, it does not require to be removed, and in no way interferes with the brilliancy of the prints, but has proved advantageous in avoiding the expense of interleaving. It seemed possible that the high-melting-point ceresins mentioned by the Author might prove quite useful in this respect.

Another aspect to which he had intended to refer had been dealt with very ably by Mr. Jackson, but he did not think that it could be over-emphasised—namely, the question of the heating of wax. The Author had stated that a temperature of 100° C. was satisfactory, and he quite agreed that this should be considered as a safe maximum temperature, and that

the use of steam of no greater equivalent temperature was probably the most satisfactory method to adopt. The use of high-pressure steam for accelerating the melting of wax was unjustified, and would only be attended with disastrous results. In order to accelerate the melting of wax, the heating surface, and not the temperature, should be increased. Some people had to use gas and others electricity, and in these cases there seemed to be great lack of proper design of the heating baths for wax, and there was ample room for improvement. Manufacturers who required to use wax in the molten state would be very glad, he thought, to have assistance and advice in this direction. Personally he thought that the heating area should be as large as possible, and that the heating medium should be incapable of producing a temperature exceeding 100° C. anywhere in the bath even when it is quite empty. Although most processes involve agitation of the wax, serious consequences do arise when working intermittently and with no automatic check on the heating. In one particular case, he said, the temperature of a bath of wax had risen from 65° C. to 150° C. in the course of a few minutes, and this was quite sufficient to destroy all efforts made by the refiner to produce a high-quality wax.

Speaking more particularly with regard to paper-waxing machines running at normal speeds, he knew of instances where, due to the uncontrolled temperature of the bath, there had been considerable difficulty experienced at times in waxing the paper. As soon as the high temperatures were eliminated, the trouble immediately disappeared. Again, he thought perhaps some manufacturers had not appreciated sufficiently the significance of the melting-point, apart from that of price. In one particular instance it was demonstrated that by using a wax having a melting-point only 5° F. higher, it was possible to increase the output of the machine by over 40 per cent. That was a very important factor, and he thought that the speed of many paper-waxing machines to-day was largely limited by the melting-point of the wax used and the temperature of the bath. If manufacturers realised the necessity of controlling the bath temperature more accurately and the possibilities of using higher-melting-point wax, they could increase the output of their machines appreciably.

With regard to the spraying of wax, he would like the Author to give a little more information on this matter. From his own experience in spraying wax by means of compressed air, he had come to the conclusion that it was impossible to produce a thin uniform film of wax which was sufficiently continuous as a surface-coating to be completely satisfactory for retaining liquids. He would like to hear whether the spraying of the cartons was effected by atomising the liquefied wax through a very small jet by virtue of the pressure alone, or whether the wax was atomised by compressed air, leaving the jet in fine solid particles in a similar way to that illustrated by the paraffin fog sprayer?

In conclusion, he would like to refer to a different aspect which was perhaps a little outside the commercial scope of the paper. Under the heading "Petroleum Ceresins," the Author referred to two papers in connection with a statement that paraffin wax contains cyclic compounds. This suggestion is comparatively new, and must arouse the interest of those engaged on research concerning the chemical constitution of wax. In the first of these papers, Yannaquis described a series of waxes distilled under

cathodic vacuum and examined by *X*-ray and petrological analysis. Amongst other evidence, he refers in particular to the existence of two distinct forms of crystal structure in these waxes in support of the contention that naphthenic compounds were present.

Personally he had examined, about four years ago, some ordinary vacuum-fractionated waxes, and had discovered precisely the same two types of crystals as those so fully described by Yannaquis. He had rather cherished the idea that these dissimilar types of crystals might indicate the existence of another series of hydrocarbons quite distinct from the straight-chain variety. More recently, however, he had been fortunate in obtaining a number of pure synthetic hydrocarbons (C_nH_{2n+2}) ranging from C_{24} to C_{34}, and a microscopic examination revealed exactly the same two types of crystals, so that his own ideas were completely shattered, and he feared he could not subscribe to Yannaquis' view. Also, on crystallographic grounds alone, the two systems which Yannaquis concluded belonged to a different series, partly owing to the fact that one system possessed straight extinction and the other oblique extinction, he believed could very well be explained by the fact that an orthorhombic crystal must of necessity exhibit those phenomena if bounded by the 310 or 110 faces. As the two different types to which he had referred were bounded by these faces, he felt that the optical evidence put forward by Yannaquis was not sufficiently conclusive to prove the presence of cyclic hydrocarbons. It would have been interesting if he had given the refractive index and specific gravity values.

In the second paper quoted, Muller and Pilat endeavoured to support the conclusions arrived at by the previous Author, but he would like to point out that their wax preparations were not distillates of a similar boiling-point range, but were prepared from an asphaltic residue by extraction, and it would be observed in their paper that the refractive indices and specific gravities were extraordinarily high in relation to the published data of straight-chain hydrocarbons. He did not think that Muller and Pilat had worked with anything like similar material to that which Yannaquis used.

Mr. D. Allan said his experience was chiefly confined to the use of paraffin wax as a candle-making material. He was certainly interested in petroleum ceresin from the point of view of its anti-mottling qualities, but he was not yet sure that, from a candle-making point of view, it had fulfilled the requirements of the candle-maker. There were anti-mottling mediums of which a proportion of 0·1 per cent. was quite sufficient to prevent any mottling and to make quite a clear candle, whereas he had not been able to produce anything of that description with three times as much petroleum ceresin. With regard to its other applications, it might quite well be that the alteration of crystal size might have the effects claimed for it. In the case of candle-making it was seldom that one was interested only in preventing anti-mottling in 135/140° wax; more often a mixture was used, which might contain paraffin scale, for example, and in that case ceresin had little or no effect, but other anti-mottling materials did have the effect of enabling one to mould a perfectly satisfactory candle without any trouble.

Mr. S. T. Minchin said that he noted that the Author stated that it was necessary for wax to be odourless and tasteless when used for the impregna-

tion of paper. Personally he had to confess that he had never yet come across a really odourless wax, in spite of the fact that some waxes were definitely put on the market with a guarantee of being odourless. He would like to hear the opinion of other people on that point. If they had found an odourless wax he would like to see a sample of it, and he would also like to know whether there was any definite test or any definite procedure that could be recommended in this connection that did not depend largely on the personal opinion of the "taster." He did not mean to infer that the odour of wax was necessarily detrimental to its use; it was not, but there was always odour present, and it seemed to him that it was very difficult to tell when the typical waxy odour passed into a very slightly oily odour. It was his experience that the wax "tasters" were very hard put to it to tell whether a wax was odourless or not, and certainly could not guarantee it was sufficiently "odourless" for all conceivable purposes any more than a tea taster could guarantee a tea to suit all palates.

With regard to the statement in the last paragraph of the paper, where the Author mentioned Assam, Burmah and East Indian waxes as having initially a pronounced tendency to crystallise strongly, he did not know how the Author had come to that conclusion. Personally he did not think one could be so certain with regard to classification as to say that these waxes showed a strong tendency to crystallise. Superficially, of course, it was not an important point, but it was well known that when abstractors or authors found such statements in a paper, they put them into their abstracts or books and they became accepted "facts."

He was very much interested in petroleum ceresin, and would throw out a suggestion to the Author that the degree of the effect was probably a direct function of the molecular weight of the added material. There was an advantage in the fact that the petroleum ceresin dealt with by the Author was completely soluble in paraffin wax, and that it was also inert, but he would be interested to hear whether the Author had tested petroleum ceresins of different setting-point and of as nearly as possible the same oil content, and, if so, whether he had noticed any difference in the potency of the effect.

Major T. R. H. Garrett said he would like to ask the Author, with regard to the more stable sample of petroleum emulsion he had exhibited, how long it had been prepared and whether he considered that such an emulsion containing, say, 8 per cent. of paraffin wax with a stabiliser would remain stable longer than an emulsion containing, say, 8 per cent. of a spindle oil.

The point of his question would doubtless be realised. At the last meeting Dr. Martin had suggested that one of the reasons, possibly the main reason, for using petroleum washes as insecticides was to suffocate the parasites and their eggs. If the emulsion to which he had just referred would remain stable longer than a spindle oil emulsion, it would obviously be a very great advantage.

There was one little point to which he would like to refer, which showed that the use of wax for preserving fruit is an old one. When coming home on leave from the Dutch East Indies in 1908 he wished to bring some Mangosteens (*Garcinia mangostana*) if it was at all possible. Mr. J. Kewley

made him some paraffix wax in the laboratory. He bought the Mangosteens in Colombo, dipped them in the wax and brought them home with great success.

Mr. A. Wolf asked if the Author had performed any experiments on the addition of relatively large proportions of petroleum ceresin to the blended wax used in the manufacture of polishes, not only with a view to reducing the tendency of the wax to crystallise, which was one of the great difficulties in polish manufacture, but also with a view to increasing the polishing properties and producing a better glaze from the finished product. Was it possible to use petroleum ceresin as a substitute for the vegetable waxes which were at present used for this purpose? There was a very great difference in price in favour of petroleum ceresin, and, if it could be used as a substitute for some of the animal and vegetable waxes, the cost of manufacture of wax polishes would be very considerably reduced.

He would like to endorse very heartily the remarks of previous speakers with respect to the oxidation of paraffin waxes. He thought there was some excuse for manufacturers, because the very term "paraffin" meant "having little chemical affinity," and it was not unreasonable to suppose that, owing to its consisting almost entirely of paraffin hydrocarbons, *i.e.* of fully "saturated" hydrocarbons, paraffin wax should, of all petroleum products, be most resistant to oxidation. That was true up to a point, but one did get oxidation in time, and it occurred not only in the presence of metals as such, but also in even greater degree in the presence of the oxides of metals capable of forming both higher and lower oxides, *e.g.* copper, manganese and cobalt oxides. Such oxides and certain of their organic acid salts were powerful oxidation catalysts, advantage being taken of this phenomenon in the manufacture of paints and varnishes, to which they were added as "driers." Turpentine, which had a well-known accelerating action on the drying of linseed oil, etc., was also capable of catalysing the oxidation of paraffin wax, especially at temperatures above 100° C., and an important paper was published in the *Journal of the Chemical Society* in about 1920 describing researches carried out at Bristol University on this very reaction.

Prior to this he himself, with research assistants, had carried out a lengthy series of experiments on the oxidation of paraffin wax at temperatures of the order of 100–120° C. by means of air containing some 500–600 parts per million of ozone. It was found that ozonised air (which was already at that time in commercial use for the bleaching of certain animal and vegetable oils, fats, and waxes) was a powerful oxidant, and that after a period of some 12–24 hrs. as much as 60–70 per cent. of the paraffin wax could be converted into organic acids of a fatty character capable of forming hard, freely-lathering soaps.

Paraffin wax of 135–140° F. melting-point derived from Burmah crude petroleum was used for these experiments. Owing to the particularly high price at that time prevailing for hard fatty acids, the process might have been of considerable commercial importance, but unfortunately it was found impossible by economic means to remove the aldehydic bodies to which the oxidised wax appears to owe its coconut-oil smell.

It is of interest to observe that the oxidation of paraffin wax by ozonised

air is accompanied by a "period of induction" lasting several hours, during which no appreciable acid formation occurs. After that it proceeds steadily. This has also been observed to occur with linseed oil. Just as paraffin wax, despite its saturation, becomes oxidised after prolonged contact with air at moderately high temperatures, so petroleum white oils, which (owing to intensive refining) are also practically fully saturated, also oxidise under similar conditions, and hence in Germany are often condemned as transformer oils despite their conforming with the B.S.I. Sludge test.

Captain W. H. Cadman said that he would like to ask the Author if he knew whether paraffin wax was a suitable material for the preservation of eggs, and, if so, how it compared with other things, such as waterglass, for this purpose.

He would also like to know whether the Author could give any idea as to the quantity of paraffin wax that was utilised in the United States in the manufacture of chewing-gum; and in this country for wax figures such as those exhibited at Madame Tussaud's.

He had noticed that in several research departments dealing with the design of ships most valuable work was done with large-scale models in which wax was used, and he would like to ask the Author whether it was paraffin wax that was used for that purpose or whether it was beeswax, or a mixture of the two.

There was one article amongst the exhibits which was of special interest at the present time, viz., the carton impregnated with wax for the distribution of clean milk. He had noticed quite recently that this type of container had been accepted by medical and health authorities as being sterile, and therefore perfectly suitable for the distribution of tuberculin-tested milk, as well as being preferable to cans or bottles for general milk distribution. The carton is cheap and is destroyed after use. The universal adoption of sealed-paper containers impregnated with pure paraffin wax would be a real safeguard for the consumer against most of the dangers from dirt and bacterial infection of milk for which the cow is in no way responsible. It would also be welcomed as a new use for paraffin.

Mr. C. I. Kelly stated that the question of the odour of paraffin wax interested him, and the remarks made on this subject by one of the previous speakers had recalled some conclusions he had reached some time ago. It was true to say that an individual who was compelled to work continuously in an odorous atmosphere undergoes a process of self-anæsthesia in relation to that odour—that is, it was possible for one to become oblivious of a certain odour after exposure to it for a very short period. At the same time, the sense of smell would be sufficiently keen to detect any other odours which were introduced at off times. For that reason, a chemist in a paraffin-wax laboratory would not be completely conscious of the characteristic odour possessed by paraffin wax; so that if he was asked to give the full inspection data of a sample of paraffin wax he might put the answer "nil" against the query "odour," but most likely he would reply that the odour of the sample was "O.K.," meaning that there was nothing unusual about

it. Nevertheless, the view of a previous speaker was tenable, that refined paraffin wax had a definite odour.

The development of an unusual odour by waxes during their handling by various industries was another aspect of the odour question. In this connection he could recall one very striking example that occurred many years ago of a chocolate manufacturer who utilised wax-proof papers for the packing of chocolates. A large batch was returned owing to a peculiar taste which they had acquired. During the investigation of the cause it was found that the wax which had been used smelt quite distinctly of something very similar to coconut fatty acids, a not unpleasant sweet odour in itself, but which, unfortunately, had an objectionable effect on the chocolates.

Whilst it is always dangerous to generalise from one isolated observation, nevertheless, his view was that the temperature to which the wax had been heated, alone, was not a particularly important factor; the other two factors which came into play were, firstly, the mass-volume ratio of the heated wax—in other words the surface area. A given quantity of wax offered to the air for oxidation—and secondly, the time during which it had been exposed to the air at this temperature. In this particular instance the wax had been dripping over the outside of the pan into the tray beneath, and the diligent workmen had returned this wax to the pot. This "recovery" cycle had no doubt been responsible for the production of the coconut-like odour, and the acquired odour of the whole batch of wax was undoubtedly the cause of the chocolates having become tainted.

He could think of only one application which the Author had not mentioned. He had in mind its use for the preservation of valuable objects of art. These were the very fine mural paintings in the Administration Buildings of Balbao, in the Panama Zone. They were valuable because they were the only existing pictorial records of the construction of the Panama Canal. The atmosphere in that neighbourhood, he believed, had a detrimental effect on fabrics, wood and vegetable matter in general, in that the air was laden with fungus spores. The pictures to which he had referred had shown signs of deterioration with this form of attack. Several methods were tried and rejected, but it was found finally that the best way of preserving them was to apply to the renovated paintings a thin coating of paraffin wax containing a very small percentage of thymol—a discovery, by the way, made by the Keeper of the British Museum in London.

Mr. P. G. Higgs, in replying to the discussion, thanked all those speakers who had suggested fresh uses for paraffin wax. The development of new applications was, of course, important, but further outlets, individually involving large quantities of wax, could not be expected to arise at will. He thought that at present due attention should be given to uses, each of which might consume only a little wax, *e.g.*, in the form of emulsions or solutions, but which might collectively lead to a considerable off-take.

He was glad that several speakers had agreed with him as to the danger attaching to the injudicious heating of paraffin wax. When checked by ordinary methods, the temperature reached in the wax bath afforded no indication of what was really happening. It was quite usual to put some sort of thermostatic control into the bath, and the user would then feel

quite satisfied that he was controlling his temperature adequately. He was quite persuaded that he had done all he could to prevent oxidation; but, of course, the thermostatic element merely measured the temperature in its immediate neighbourhood, and, unless some sort of circulation of the wax were provided, it was quite impossible even to guess at the temperature in other parts of the bath.

Mr. Scott-Harley had made a very interesting addition to the statements in the paper as to the constitution of wax. The papers to which Mr. Scott-Harley had referred, in which it was stated that paraffin wax itself might contain naphthenic components, had been mentioned merely to make the point that very little was known about paraffin wax itself; even less, then, could be said about the petroleum ceresins, which are obviously more complicated. People had been brought up to believe that paraffin wax was a mixture of normal paraffin hydrocarbons, but he thought it probable that this idea would have to be modified.

The spraying of wax is carried out by two methods: firstly, the wax is itself under pressure and is pumped through a jet, *e.g.*, in the waxing of cartons and butter-boxes; and secondly, compressed air may be used, as, for instance, in the treatment of citrus fruit. In the latter instance, the fog effect referred to by Mr. Scott-Harley was deliberately sought.

He quite agreed that the choice of setting-point by the user should be considered more carefully than it was at present; it should not be always subordinate to the cost.

He was rather disappointed to hear of Mr. Allan's unfavourable experience of the use of petroleum ceresins in candle-moulding, but he could only say that in certain cases they did seem of some value.

Mr. Minchin and other speakers had referred to the question of odour, which was a very controversial one. Technically, the presence of a very slight odour could not be really harmful. In any case, the conditions of use nearly always quickly nullified all the care that was taken to make the wax as nearly odourless as possible; after a very short period of service it usually had sufficient odour to be turned down by any wax chemist, whatever his method of testing might be.

Reference had been made to his statement that Assam, Burmah, and East Indian waxes had a pronounced tendency to crystallise strongly. He granted that it was wrong to have been so definite, but he thought that it was generally known from ordinary observation that some waxes, when fractured, showed a much more definitely crystalline structure than others. He was, of course, only judging waxes macroscopically, and was not entering into the difficult subject of their microscopy.

In connection with the doping of paraffin wax he had certainly tried petroleum ceresins with different setting-points, and their effect seemed to be of much the same order as that of the ceresin in which he was particularly interested. He would hesitate to say anything with regard to ceresins of different oil content. For one thing, it was extremely difficult to estimate the oil content of a ceresin and, so far as he knew, there was no method which claimed to do so.

In reply to Major Garrett, he would say that the emulsions which had been shown during the meeting had been made about three weeks before.

They were of several types as regards stability, *i.e.* tendency to cream out into lumps which cannot be easily re-dispersed.

The ammonium oleate emulsion was a typical coarse dispersion which creamed relatively quickly; after creaming, it formed solid lumps much more quickly than did the fine dispersions, which had been made mechanically. Of the latter, the casein-stabilised emulsion which he had shown seemed to be the most stable. The fact that its particles were of the same order of size probably accounted for this. The potassium oleate emulsion was not quite so stable; its particles were all very small, but the size distribution was much wider than in the casein emulsion. He could not say whether these emulsions might be used as horticultural sprays. He imagined they would give rise to difficulties, owing to the formation of a film or collection of wax on the foliage after drying.

A wax emulsion would break in a different way from an oil emulsion. In an oil emulsion the particles ran together, giving a layer of liquid, whereas in a wax emulsion the particles could not coalesce because they were solid; they simply flocculated and formed a more or less continuous layer of wax.

Major Garrett said he was referring to winter spraying, so that the question of spoiling the foliage did not arise; with regard to the mode of breaking, when the wash had dried the whole effect was over in any case, and the story was finished.

Mr. Higgs agreed that, while he had had no experience in this direction, the suggested application certainly seemed promising.

In reply to Mr. Wolf, he said that the polishing qualities of petroleum ceresins were not particularly good, so that these materials could not advantageously replace the commonly accepted waxes for polish-making. The effect of a very small proportion of the ceresin was another matter, and was purely structural. That effect was obtained even in the presence of beeswax and carnauba wax. Carnauba wax itself had a somewhat similar gelatinising effect, but the stability was not so good as when a little ceresin was present.

The possibility of using paraffin wax as an egg-preservative instead of waterglass had been suggested, but this had in fact been tried in the past. He thought that the reason why the practice had never become popular was the fact that it was a purely domestic operation. The housewife undoubtedly thought that waterglass, in spite of its disadvantages, was easier to manipulate and more convenient than molten wax. Paraffin wax was certainly used in large quantities in the manufacture of chewing-gum, though he could not say to what extent; it was entirely a commercial question.

High-class modelling wax usually consisted of beeswax, either alone or in admixture with paraffin or other waxes. Paraffin wax by itself was not suitable, owing to its fragility at ordinary air temperatures.

On the proposition of THE PRESIDENT, a hearty vote of thanks was accorded to Mr. Higgs for his very interesting paper, and the meeting then terminated.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

A GENERAL Meeting of the Trinidad Branch of the Institution of Petroleum Technologists was held at Apex Club, Fyzabad, on Wednesday, 28th February, 1934, Mr. G. H. Scott, B.Sc., Branch Chairman, in the Chair.

The following paper was presented :—

ECONOMICS OF PUMPING AND GAS LIFT.

By T. W. DAGG, M.A. (Member).

The object of this brief paper is to enumerate some of the principles involved in the choice of pumping or gas lift as alternative methods of artificial lift, in order to bring out by discussion the experience of different fields.

From time to time many advantages have been claimed for different modifications of both forms of lift, and although these have been advantageous in certain localities or individual wells, they have proved to be uneconomic when applied to other localities.

It is now desired by discussion to elucidate some of the reasons for the non-realisation of some of the claims, and to form a basis upon which the choice of artificial lift may be determined for a particular well or area.

For the purpose of discussion, it is suggested that the term pumping will apply only to plunger pumping, and where displacement pumping is implied, it will be mentioned specifically.

A certain amount of confusion exists at the present time in the actual nomenclature of the different stages of gas lift in the artificial lift period of a well. It may therefore be stated that the terms "straight" or "continuous gas lift" apply only to that period when continuous flow is being obtained by injecting gas into the tubing or annular space between tubing and casing.

The term "intermittent gas lift" applies only to that stage when periodic flow is being obtained by injecting gas *at intervals* under the same conditions as for continuous gas lift in that the tubing is open at the bottom. "Displacement pumping" applies to that period when oil is lifted from some form of chamber which fills by rise of fluid level and is closed against the formation as oil is ejected.

In deciding upon an artificial lift programme for a field, there are many factors which must be taken into consideration, and it is only by apportioning to each factor its due importance that the more economic system of lift can be determined. It is usually impossible to obtain sufficient data from tests on individual wells, in that the time which must elapse while test wells are being produced to their economic limit is too long to await a decision on the form of artificial lift to be adopted. Short-duration tests are often effective in enabling a decision to be arrived at on some of the

factors involved, but experience on some of the fields in the Maracaibo Basin has proved that it is wrong policy to decide upon artificial lift programmes solely on short-duration tests. At least one instance can be quoted of heavy additional expenditure being incurred in a change of programme from displacement pumping to plunger pumping in the later stage of artificial lift.

It is therefore essential that artificial lift programmes should be based largely on the experience of similar types of fields which have reached a much later period in their production life than the particular field in question. Inasmuch as the conditions which prevailed in Seminole in 1927 were particularly suited to straight gas lift, excellent results were obtained and an impetus was given to the adoption of gas lift in many of the producing fields of the world. It is now therefore possible to obtain data over long periods of the two forms of lift, and from this many useful inferences may be drawn. It is suggested that the choice of artificial lift for an individual well, locality or field be based on the data available under the following headings not necessarily in order of importance:

I. Mechanical Condition and Verticality of Holes.

Obviously plunger pumping in a very crooked hole is uneconomic due to excessive wear on rods, tubing, and casing. Therefore, before deciding on an artificial lift programme it is essential that all wells from which deviation record are not available should be surveyed and logs made showing the deviation at different depths.

It is difficult to lay down a hard-and-fast rule as to the degree of deviation which makes plunger pumping uneconomic, but comparison of many cost figures from various fields indicate that $2\frac{1}{2}°$ per 1000 feet of hole is the maximum for which it is desirable to pump wells with plunger pumps.

The wear and tear on sucker rods and tubing can be considerably lessened by the use of sucker-rod protectors, which should be made of wood rather than metal, since the latter may cause continual shut-down due to filings clogging the pump valves. A long, slow pumping stroke also alleviates to a certain extent the wear on sucker rods in crooked holes, but this is not always possible where wells are pumped from a central pumping power.

One instance can be quoted where the life of sucker rods was increased 200 per cent. by decreasing the number of pumping strokes per minute from 20 to 12. Production was maintained constant by increasing the size of the pumps and using a longer pumping stroke.

Close investigation of many pumping records has shown that wells with a large degree of deviation can be pumped economically provided that the deviation is regular. A sudden deviation due to side-tracking when drilling has been shown to cause more sucker-rod trouble than a regular deviation of double the amount.

II. Sand Conditions.

It is essential that sandy wells should, if possible, be gas-lifted. The actual percentage of sand which makes pumping wells uneconomic is difficult to state arbitrarily without taking into consideration the viscosity of the

oil to be pumped and the nature of the sand. Instances can be quoted of wells making a very low percentage of a particularly abrasive sand which were uneconomic to pump, and other instances can be quoted of wells pumping viscous oil economically with high sand content.

In displacement pumping of very sandy wells difficulty has often been caused by sand settling on the chamber valve and preventing free access of oil. However, this difficulty has to a great extent been overcome by the adoption of the mushroom type of valve with a large fluid passage, and so designed that only a small static head is required to open it.

III. Viscosity and Specific Gravity of Oil.

It has been claimed by advocates of gas lift that a high-viscosity oil assists the piston or slug action in displacement pumping, and that better lift efficiencies can be obtained with high- than with low-viscosity oil. However, investigation and the results of many experiments on the subject, particularly in the fields of the Maracaibo Basin, have indicated that in practice the assistance given by piston effect is more than counterbalanced by the extra energy required to force a high-viscosity oil through a very narrow-diameter tubing at a high velocity. Very close comparisons of intake gas–oil ratios showed that where the same energy was available for lifting the oil, a higher lift efficiency was obtained with less viscous oil for average velocities through different diameters of macaroni tubing.

In straight gas lift, provided that the tubing used is of sufficiently large diameter, high lift efficiencies can be obtained with high-viscosity oil. In plunger pumping with a high-viscosity oil the chief difficulty lies in the possibly increased amount of sand carried in suspension.

A series of experiments carried out in the Mene Grande Field, Venezuela, with the object of ascertaining the effect of viscosity on lift efficiency indicated that, in a straight gas-lift well for a fixed diameter of tubing and the same velocity, the lift efficiency was directly proportional to the viscosity up to the point where the effect of slippage predominated. Therefore it may be said that high viscosity is no deterrent to the use of straight gas lift, provided that the design of the tubing is correct and that in displacement pumping a comparatively poor lift efficiency will be obtained.

IV. Natural Gas–Oil Ratio and Availability of Gas for Gas Lift.

Where natural gas–oil ratio is high, it is, of course, more economic to use gas lift than plunger pumping, as the large supply of natural gas available which impedes plunger pumping by gas locking assists injected gas in lifting the oil to the surface.

Where plentiful and continuous supplies of high-pressure gas are available from high-pressure traps, there is little doubt that gas lift will prove more economic than plunger pumping. In the case where gas or air must be compressed from atmospheric, and compressor installations, etc., must be provided for gas lift as against pumping powers or individual units for plunger pumping, the choice of artificial lift becomes a matter of accounting, in that construction and maintenance charges for both kinds of lift can be accurately estimated.

In general, it can be said that gas lift is cheaper than pumping by individual unit, while a pumping power is cheaper than gas lift, provided that :—

(*a*) The condition of the oil, natural gas–oil ratio and sand content is suitable for both methods of production.
(*b*) The holes are not deeper than 3000 feet.

V. Productivity and Length of Life of Wells.

The rate of production which can be obtained with plunger pumps is limited to their volumetric capacity, except in cases where the function of the sucker rods is merely that of an agitator in inducing periodic flow. The production which can be obtained by gas lift is limited only by the capacity of the well. Instances can be quoted of more than 100 per cent. increase in daily production by changing from plunger pumping to straight gas lift, but, contrary to the claims of the early gas-lift advocates, the ultimate production cannot be increased by any particular method of artificial lift. A strong incentive to the development of displacement pumping has been to provide a method of production which would enable gas-lift installations to be used down to the last stages of the economic life of wells, and thereby avoid the costly change over to plunger pumping after the straight gas-lift stage was passed, but the question requires very careful consideration from the economic point of view in every case before a displacement pumping or plunger pumping programme is decided upon.

VI. Paraffination.

In pumping wells accumulation of wax not only chokes the well by restricting the size of the oil passage, but the increased load often causes the rods to break if the wax is not removed at regular intervals. In gas-lift wells the main difficulty caused by paraffination is restriction. When gas expansion is used as the lifting medium for oil a definite cooling results from the expansion of the gas. This cooling cannot be avoided, but by itself is usually too small to cause much trouble from paraffin, provided that only sufficient gas is injected to lift the oil. The increased velocity of gas and oil in the tubing where excess gas is used is also a deterrent to the deposition of wax.

The most serious trouble encountered from deposition of wax in plunger pumping wells occurs when the pump acts merely as an agitator in inducing periodic flow, and after wells have become settled pumpers, the difficulties of paraffin accumulation decrease.

VII. Tendency for Emulsification.

Where it is necessary to produce water with production, the choice of lift depends largely on the method which will cause least agitation of water and oil in contact.

In plunger pumping it has been found that a long, slow pumping stroke has decreased the emulsion formed, and in gas-lift wells it has been found that decreased flow velocities have acted favourably.

Many other minor factors must be taken into consideration in deciding on an artificial lift programme, such as the availability of labour and supervision which it is contended must be more skilled for gas-lift than for plunger pumping.

It is hoped that discussion will reveal other points not mentioned.

In conclusion, it is stated that although plunger pumping and gas lift are alternative methods of artificial lift, there are many fields and localities which from the economic point of view are only suited to one or other method of lift, and wrong application can only result in unnecessarily high lifting costs.

DISCUSSION.

Mr. A. Frank Dabell said from recent experience he was able to confirm the declaration by the Author that where gas–oil ratio was high it was economical to use gas-lift rather than plunger pumping; and he ventured to suggest that eventually gas-lift would displace plunger pumping entirely.

If, contrary to the claims of the early gas-lift advocates, ultimate production could not be increased by any particular method of artificial lift, then, given identical conditions, he considered it better to practise earlier gas lift, mainly for the reason that the oil was more quickly brought into possession.

It was held that, inasmuch as the energy required to bring oil to the surface was represented by the sum of the energy required to bring oil into the hole plus that required to lift the oil to the surface, by supplementing the lifting energy by gas from an extraneous source, more energy was left to bring oil to the hole.

He asked the Author if he could justify this contention.

Mr. M. A. ap. Rhys Pryce said that he thought the last paragraph of the paper was one of the most important statements made. He did not know if the members present had had the same experience; in the fields in which he had been there had usually been the gas-lift expert and the plunger-pumping expert, and the speaker had always held that production engineers as a whole should be equally versed in both branches of artificial lift before they could be termed production engineers, otherwise there was the tendency for the individual to be biassed in favour of one form of lift or other and allow his preferences to sway his judgment.

He was interested in the Author's statement that data from various fields indicated that it was economic to pump a well that was off 2½° per 1000 feet; that meant 7½° off at bottom for a well 3000 feet deep. This corresponded with his own experience, but he had seen wells worse than that, that were economical to pump. This brought them to the question as to whether, apart from correlation purposes, the straight-hole drilling to the extent it was generally carried out at present was not going a little too far from the point of view of economic operation. Straight holes were asked for firstly by the production engineers on account of crooked-hole conditions in pumping, and secondly by geologists for the purpose of correlation. He invited the Author's opinion on that point.

Mr. K. W. G. Patterson said, considering the various factors brought out by the Author in his paper, as he held they were more or less general principles governing that question, he thought that artificial lift methods should be even more clearly defined by classifying such methods according to the fundamental reasons for their adoption.

He thought that the natural stages of production were :

1. Sufficient energy to drive oil to the bottom of the hole, and the necessary bottom-hole pressure to support and maintain a column of gas–oil mixture under conditions of flow;
2. Sufficient energy to drive oil to the bottom of the hole and a bottom-hole pressure great enough to support a column of gas–oil mixture extending to the surface, but not great enough to maintain such a column under conditions of flow without an additional supply of energy from the surface;
3. Sufficient energy to drive oil to the bottom of the hole, but bottom-hole pressure too low to support or maintain a column of gas–oil mixture extending to the surface under any conditions;
4. Insufficient energy to drive oil to the bottom of the hole.

If production methods were classified under the above principles one would have :

1. Flowing. Well head and tubing control;
2. Straight gas lift with intermittent lift as a secondary stage;
3. Re-pressuring (may be equally well put before the straight gas-lift stage);
4. Plunger or displacement pumping;
5. Gas drive (may also be equally effective at an earlier stage).

Re-pressuring and gas drive were not within the title of the paper, but it was obvious that the probable success or otherwise of those methods had an important bearing on any economic comparison between gas lift in a general sense and the purely mechanical method of producing oil.

In considering the economic aspects of gas lift and pumping, it should always be kept clearly in mind that straight gas lift was fundamentally an earlier stage method than plunger pumping.

If after the flowing stage there remained sufficient oil in the sand for commercial production, there must follow for the great majority of wells under gas energy control the second stage, under which wells would react to straight gas lift.

Economically the important comparison to be made was between displacement pumping and plunger pumping which came under the same producing stage.

If displacement pumping could be proved to be an adequate substitute for plunger pumping, the gas-lift method was unquestionably the most economical, as all pressure equipment could be utilised right down to the dry-hole stage.

If displacement pumping for reasons peculiar to the field could not be employed efficiently, the feasibility of adopting straight gas lift at the earlier stage would depend, as had been pointed out in the paper, on the volume and consistency of trapped gas available.

If no natural high-pressure gas was available, then the cost of the necessary

compressor station and gas-distribution system would have to be paid for, and a profit obtained before the wells passed out of the straight gas-lift stage, unless the same equipment could be adapted without much additional expenditure to other oil-field purposes, such as gas drive, re-pressuring, and gas collection.

Hitherto a big item of expense in displacement pumping had been the necessity for using two strings of tubing. The recently developed method of the plunger lift did away with that disadvantage, and at the same time overcame the severe obstacle of requiring to run practical-sized chambers into wells mechanically unsuitable for the purpose.

From the point of view of capital cost the central pumping power compared favourably as a general scheme, but could not compare in flexibility and economy of operation with the employment of high-pressure gas if that method was planned from the early life of the field.

Mr. G. A. Walling suggested two other factors for consideration. The first was the question of terrain and topography, surface conditions, etc. In the second place, he did not think the Author had pointed out that gas lift fitted in very well with any re-pressuring schemes that might be contemplated, because the two schemes could be worked together, and that would tend automatically to reduce operating costs.

Displacement pumping was introduced primarily as a measure to follow on after the gas-lift stage had ceased, but it really went further than that under certain conditions. The change from the flowing stage direct to the displacement-pumping stage could be effected in a field with shallow wells.

Where shallow wells which had a low formational gas–oil ratio could be flowed down to 150–200 barrels per day, they could be converted to displacement pumping with lower lifting ratios than could be obtained with straight gas lift, and costs would be correspondingly reduced.

As already mentioned in the paper, a high formational gas–oil ratio assisted straight gas lift, since it meant that less gas had to be supplied from the surface to maintain flow. When the straight gas-lift stage had been passed, conversion to displacement pumping did not take advantage of the energy in the formational gas for assisting to raise the oil to the surface, and the whole of the energy had to be supplied from the surface.

Application of displacement pumping to deeper wells resulted in high lifting ratios where the lifting medium was exhausted from the two tubing strings during each cycle. The addition of a device in the bottom-hole chamber to conserve part of this energy would reduce the lifting volume required, but further complicated the system. Pumping very often took some advantage of the energy in the formational gas, inasmuch as lift was sometimes obtained by agitation rather than by straight displacement. An installation where a plunger was operated by gas either from the well itself or with the addition of gas from the surface appeared to exploit the available energy from the formation more efficiently. If, however, sub-surface conditions were such as to cause excessive wear of any moving parts in the well, it would be advisable to employ displacement pumping, even though its lifting efficiency were lower.

He directed attention to the Author's statement that in general in wells down to 3000 feet gas lift was cheaper than pumping by individual unit,

while a pumping power was cheaper than gas lift, provided that "the condition of the oil, natural gas–oil ratio, and sand content is suitable for both methods of production." He thought that the comparison in costs was dependent on the life of the well and how long it had to be operated.

Probably the shorter the life of the well the cheaper would be plunger pumping compared with gas lift, because the lower capital expenditure for pumping equipment would more than counterbalance the higher maintenance costs which are usually associated with pumping as compared to gas lift. If the wells were to be produced for long periods, gas lift would compare more favourably with pumping.

Mr. J. W. Hardy said there was one point in the paper with which he did not agree. The Author stated that "high-viscosity oil assists the piston or slug action." Their experience had been rather the opposite. A low-viscosity oil rising in a slug through the tubing wetted the tubing with a thin film, but a very high-viscosity oil clung to the tubing and left a blanket of oil as it rose, so much so that the slug was considerably shortened by the time it had reached the surface. Also, the gas might break through, causing loss of the slug effect.

There was no mention in the paper of using compressed gas as a source of power to drive a plunger pump. He believed that was done recently in America, and it gave very successful results, because it enabled a long, slow stroke to be imparted to the rods; when used over rough country it was a very convenient source of power at the well. He knew that the use of compressed air or compressed gas as a source of power was regarded as inefficient, but he did not think it could be more inefficient than the average displacement pump.

Mr. L. C. Stevens quoted the Author's reference to the adoption of the mushroom type of valve for overcoming the difficulties experienced in displacement pumping of very sandy wells. He said that his displacement pumping experience was confined to one field, but they had found that the mushroom type of valve had not given such good service as an ordinary ball-and-seat type valve, while the mushroom type of valve had a much greater seat area and should give freer access of fluid, the chief cause of trouble in a sandy well was the cutting action of the sand on the valve and seat. The mushroom type of valve was made of a brass alloy that did not stand up to the sand abrasion like the ball-and-seat type, the manufacturers of which had had more experience in the production of materials for difficult well conditions. Further, the ball-and-seat type of valve had a better self-cleaning action than the mushroom type; the collection of sand on top of the valve increased the static head required to force the oil into the chamber, and sand round the rim of the seat prevented the valve from seating properly. They had adopted a standing valve for displacement pumping made from an ordinary ball-and-seat which was run on the end of the macaroni and seated in an ordinary pump shoe fixed on the bottom of the chamber. This enabled the balls and seats to be examined without pulling the outer string of tubing, and the standing valve could be raised and any accumulation of sand blown out. This was a great advantage over the mushroom-type valve.

He wished to mention that in connection with the exhaustion of gas from a gas displacement well at the end of a shot, if operating without a chamber valve in the well most of the expansion energy of the gas was inevitably lost. It acted like a steam engine without a cut off, except that the pressure energy of the gas was being utilised. If, because of difficult well conditions, it was desired to operate without a chamber valve, this loss of expansion energy could be overcome to a certain extent by the use of a delayed-action release valve at the surface. After the intermitting valve closed, the gas was not immediately exhausted, but was held by the release valve until it had expanded to a lower pressure than the original injection pressure. Thus when operating with a line pressure of 400 lb. gas could be injected for 2 minutes at that pressure and then cut off; it was then expanded during the next 2 minutes until it reached a pressure of, say, 200 lb., when the delayed action release valve came into operation and it was exhausted. By this means gas consumption could be cut down to as much as two-thirds or even half.

Mr. R. Godfrey invited the Author's opinion as to the most economic pressure at which to run a gas-lift system. He considered it an important point, inasmuch as tubing size and depth could be varied to suit any given pressure.

The points in favour of raising the oil to the surface as quickly as possible by gas lift instead of the slow plunger-pumping method, as pointed out by Mr. Dabell, appeared particularly applicable to boundary wells.

There were some outside features to be considered when deciding upon a method of artificial lift as suggested by Messrs. Walling and Patterson, such as re-pressuring, and the existence, or possibility of installation, of a gas absorption plant to be run in conjunction with the wells.

If gas lift was adopted, compressors could be transferred from one service to another (gas collection, gas lift or re-pressuring) merely by changing cylinders, to meet the various demands throughout the life of the field, and would result in a minimum capital expenditure on compressor equipment.

Mr. W. G. C. Tomalin congratulated the Author on a very excellent paper. On reading it through he gained the impression that, in general, he compared gas lift with pumping. By gas lift was generally understood the injection of gas into a well with a high fluid level as a means of prolonging flow after natural flow ceased. It seemed to him that from the economic point of view a better comparison could be made by comparing displacement with plunger pumping, and he did not think this point was sufficiently discussed in the paper.

Artificial gas lift could be applied in most cases only for a short period, and then fluid levels in a field tended to fall, and one had to employ some other method; generally the plunger pump was resorted to. His Company had studied the economics of the displacement pump as compared with the plunger pump, and some very interesting facts had come to light, namely, that in using the plunger pump there was always a large percentage of time off production. Moving parts were continually wearing out, which had to be replaced, and in order to overcome this defect a very considerable amount of money was expended in labour, which generally increased the cost per

barrel of oil, whereas in displacement pumping, where there was a very slow ingress of fluid to the chamber and very few moving parts, that was not the case. It seemed to him that, in principle, displacement pumping should generally prove to be more economical.

Mr. A. J. Ruthven-Murray said that, from the Author's reference to high-viscosity oil, it would appear that he had had a good deal of experience with this in Venezuela. He invited his views as to the relative merits of plunger pumping, natural gas lift, and displacement pumping in wells having an average depth of 3000 feet, where the crude was highly viscous and attended by a low gas–oil ratio. Under such conditions he presumed that straight gas lift would be of little value.

Mr. T. W. Dagg, in reply, said the first question referred to the figure of 2½° per 1000 feet of hole as being the maximum for which it was desirable to pump wells with plunger pumps. That figure was, of course, entirely arbitrary. It was taken from a series of statistics and costs from various fields. He did not say that a well of 2° could not cause considerable trouble, nor was it impossible to pump a well of 20°; he had actually seen one well 23° off vertical which was pumped economically. The rods were examined at intervals, and the amount of wear was compared with other wells. When the actual costs were compared with those for gas lift in the area in question, the well could be considered as being pumped economically with an actual deviation of 23°. In another area of his particular knowledge there was one well in which acid-bottle tests showed an absolutely regular deviation. The well was drilled with a regular curve, and the acid-bottle readings at stated intervals showed very small alteration. This well actually was shown to have a deviation of over 30°. In this particular case it could not be said that the well was pumped economically, but it was pumped, and the required quota of oil was obtained from the well, at a cost which was only slightly higher than gas lift for the area.

The next question raised was that of slug effect. He had stated that the assistance given by slug effect in displacement pumping had been largely over-rated, and that it was counterbalanced by the extra energy required in forcing very viscous oil through a narrow-diameter tubing. He was speaking from statistics and figures from four fields, and it was interesting to know that experience in Trinidad had been different on one field, and he would very much like to have a comparison of figures on the subject.

With regard to the mushroom type of valves for sandy wells, it was claimed by the makers that they showed considerable improvement on the old ball-and-seat valve. Many experiments with the mushroom type of valve had shown that where no clay or mud or other substance which would bind sands together was present, the mushroom valve gave very improved results over the ball-and-seat, but where clay or mud was present the mushroom valve did not give equal results to the old ball-and-seat valve.

It was definitely not possible to increase the ultimate production of any well by changing from gas lift to pumping or vice versa. There was a certain amount of oil in the sand to be produced with a certain amount of

gas, and a certain amount of energy was available. If extraneous gas was introduced to lift the oil from the well it did not alter the energy available in the sand. In the case of a very depleted sand where the actual producing horizon was a matter of several hundred feet and the fluid level was very low down, it was possible to inject gas into the upper part of the sand at the same time as the well was being produced, but this was a re-pressuring operation, and any increase in ultimate production obtained in this way was due only to the fact that gas had been injected into the sand, and not to the fact that the well was gas lifted rather than produced on a plunger pump.

With reference to the question as to whether direct comparison could be made between gas-lift and plunger pumping, and the suggestion that the comparison should be between plunger pumping and displacement pumping, the Author thought that this was a very good point indeed, and one which he had expected would be raised. If a well was straight gas lifted and the fluid level was high, the production of the well would be greater on gas lift than plunger pumping, owing to the limited capacity of plunger pumps. Displacement pumping would afford comparison, in that the production from displacement pumps was limited in the same way as from plunger pumps.

On the question of producing a high-viscosity oil from a depth of 3000 feet with a low gas–oil ratio, the Author desired to point to several instances where that condition existed. Where the fluid level was high and the capacity of the well was very large, large production was obtained by using gas lift and a large-diameter tubing. The production obtained by gas lift was at least 300 per cent. greater than could have been obtained by plunger pumping, but in the later stages of the wells in question when the fluid level went down the comparison of actual production obtained was equal, but it was found at this stage that plunger pumping gave better economic results than gas lift.

The question of comparison of gas lift and pump for a very high-viscosity oil depended largely, he thought, in the first place on the actual capacity of the well, and in the second place on the fluid level which the wells would maintain. If the fluid level and capacity were high, gas lift was probably preferable, and if the fluid level was low, it became a matter of working out respective costs.

Replying to the question of the best pressure or the optimum pressure for a high-pressure gas-lift line, the Author stated that it depended entirely on the depth of the wells to be operated and the fluid levels, but he thought that a steady pressure of 300 lb. was a fair pressure for wells up to 2500 feet, but for wells 3000 to 3500 feet there should be a pressure of at least 400 lb. in the line. Rather more important than the pressure were fluctuations in the gas-lift line. He knew of cases where a 10 per cent. fluctuation of pressure in the gas-lift line caused very serious losses of production. At a later stage when displacement pumping was in use he considered that a pressure of 400 lb. should be maintained for a well 2500 feet and 500 lb. for wells up to 3500 feet.

On the motion of the Chairman, a vote of thanks was accorded to the Author, and to their hosts, the President and Members of the Apex Club, for the use of their building.

DETERMINATION OF THE AROMATIC CONTENT IN CRACKED GASOLINES.*

By J. C. Vlugter.

SYNOPSIS.

For the determination of the aromatic content in cracked products, the actual determination by means of concentrated sulphuric acid is preceded by a selective hydrogenation of the olefines. This hydrogenation usually takes place at 300° C. under high hydrogen pressure in the presence of a specially prepared molybdenum catalyst. In extremely rare cases a disturbing polymerisation occurs during the course of this hydrogenation owing to very active olefines and diolefines, which necessitates a preliminary hydrogenation at a lower temperature with a nickel catalyst.

In a saturated gasoline the aromatic content can be easily and reliably determined by means of concentrated sulphuric acid. To do this one need only shake the gasoline for some time with an excess of 98–100 per cent. sulphuric acid. The decrease in volume of the gasoline at once indicates the aromatic percentage by volume, from which one can calculate the percentage by weight by the aid of the specific gravity of the gasoline determined before and after the treatment with sulphuric acid. In some cases, as with low-boiling gasoline fractions, the aromatic content can be calculated more accurately still from the difference in the aniline points of the gasoline before and after sulphonation. Howes,[1] says, "This method for the estimation of aromatics in the absence of unsaturates seems to be capable of more reliable results than any method yet devised."

Olefines have a detrimental effect, because, as a rule, these are more easily attacked by the sulphuric acid than are the aromatics. It has been proposed, so as to eliminate and at the same time to estimate the olefines, to use less strongly concentrated sulphuric acid (of 80–94 per cent.), but it has been proved that one can never select a concentration that completely eliminates the olefines without attacking the aromatics.[2] Other drawbacks to this method are the occurrence of polymerisation reactions between the olefines themselves, of condensation reactions between olefines and aromatics, and of the formation of paraffins from the olefines [3] under the influence of the sulphuric acid. There is also the possibility that cracked products may contain aromatics with olefinic side-chains (*e.g.* styrene), which would be removed as olefines even if it were possible to make a sharp separation between aromatics and olefines by means of a moderate concentration of sulphuric acid. This elimination would then result in the loss of the aromatic part of these compounds for the further determination. This latter fact would make the results of any method of separation, whether performed with sulphuric acid or with any other reagent, more or less unreliable in the presence of olefinic aromatics.

In the Laboratory of the *N.V. De Bataafsche Petroleum Maatschappij* in Amsterdam a selective hydrogenation of the olefines is applied to remove

* Paper received Nov. 29th, 1934.

the unsaturated compounds, after which process the aromatic content can be determined in the usual manner by means of concentrated sulphuric acid. During this hydrogenation the aliphatic olefines are converted into paraffins, the cyclic olefines into hydro-aromatics, and such compounds as styrene into aromatics with paraffinic side-chains. Some time ago Waterman, Perquin, and van Westen [4] suggested this selective hydrogenation, for which they used a palladium catalyst and carried out the hydrogenation at room temperature and atmospheric pressure. Under these conditions pure olefines are completely hydrogenated and aromatics not at all. A drawback to this method, however, is that the palladium catalyst is extremely sensitive to poisons, particularly to sulphur compounds, which practically invariably occur in cracked gasolines. For this reason it was decided to make use of a catalyst immune to sulphur poisoning, notably a molybdenum catalyst [5] prepared in a particular way, and hydrogenation has then to be carried out under increased pressure. A rotating Bergius autoclave with a capacity of 2 litres (or some other high-pressure autoclave) is provided with 200 ml. of cracked gasoline and 40 gs. of the catalyst referred to above. The autoclave is closed and hydrogen pumped in until the pressure is about 100 atm. and then, in 40 to 45 minutes, it is heated to 300° C. At this temperature it is kept until the pressure, which at first decreases owing to the hydrogenation reaction, remains constant for 30 minutes. Then all heating is stopped. When the autoclave has cooled down to about 200° C. the hydrogen and the hydrogenated gasoline are allowed to escape hot through the valve of the autoclave, in order to cause an immediate separation between the catalyst and the gasoline by distillation. The gasoline is collected in vessels cooled by ice and solid carbon dioxide, and after the pressure has been released the autoclave is evacuated to remove entirely the highest boiling constituents of the gasoline.*

An A.S.T.M. distillation is made of the total reaction product and a bromine value determined (by McIlhiney's method).[6] The A.S.T.M. distillation is made in order to determine whether, besides the hydrogenation, polymerisation of the olefines has taken place. This actually did occur in one case, but this will be dealt with later. If, however, the distillation curve of the gasoline has remained unchanged and the bromine value is practically zero or less than two, the aromatic content is determined in the usual manner by means of concentrated sulphuric acid. If the bromine value is higher than two, the hydrogenation must be repeated.

Example.—A cracked distillate with a bromine value of 80, boiling from 40° to 300° C., was hydrogenated in the above-mentioned manner. The reaction product had a bromine value of 1·9, and the distillation curve had scarcely changed. The product was then shaken with 98 per cent. sulphuric acid, which resulted in a decrease in volume of the gasoline of 9·4 per cent.

If benzene is treated at 300° C. under high hydrogen pressure for a prolonged period in the presence of the molybdenum catalyst, no addition of

* If it is desired to hydrogenate kerosine or gas-oil fractions selectively for the elimination of the olefines, it is better to separate the hydrogenation product from the catalyst by filtration, after which the catalyst should be washed with a low-boiling solvent which can again be removed by distillation. In this case the contents of the autoclave need not be allowed to escape hot.

hydrogen takes place, which proves the selective hydrogenation activity of the catalyst.

As has already been stated, in one single case a disturbing polymerisation was observed as a side reaction of the hydrogenation. In this case, a low-boiling Gyro gasoline, the very active olefines and diolefines strongly tended to polymerisation under the conditions of the hydrogenation, which was apparent from the distillation curve after the reaction. In such a case a different course must be followed.

The cracked gasoline is pre-hydrogenated at a comparatively low temperature (150° C.) under high hydrogen pressure with a catalyst consisting of kieselguhr carrying about 20 per cent. of nickel,* by which process the very active olefines and/or diolefines become saturated, and thus cannot give rise to disturbing side reactions in the next hydrogenation at 300° C. with the molybdenum catalyst. Of course the possibility of aromatic hydrogenation becomes greater if a nickel on guhr catalyst is used.

Example.—The autoclave is provided with 200 ml. of cracked gasoline (Gyro gasoline) and 20 gs. of nickel catalyst, then closed and the pressure raised by pumping in hydrogen to about 100 atm. After that it is heated to 150° C. in 40 to 45 minutes and kept at this temperature until the pressure remains constant for 30 minutes. The contents of the autoclave are then allowed to escape at 150° C. (as described above). The bromine value of the reaction product is only determined for identification purposes. For the second treatment the autoclave is provided with the reaction product of the first experiment, 40 gs. of the molybdenum catalyst are added, the autoclave is closed and pressure brought up to 100 atm. In 40 to 45 minutes the autoclave is heated up to 300° C. and this temperature kept until the pressure remains constant for 30 minutes. Then heating is stopped and the contents of the autoclave are allowed to escape at about 200° C. The bromine value is determined and an A.S.T.M. distillation of the reaction product made. The distillation curve will now show little difference in comparison with that of the base material. If the bromine value is less than two, the aromatic content can be determined in the usual way with sulphuric acid. Otherwise the last hydrogenation must be repeated.

In the case of the Gyro gasoline with a bromine value of 179·3, the first hydrogenation with the nickel catalyst at 150° C. caused the bromine value to fall to 115·9; after the second hydrogenation with the molybdenum catalyst at 300° C. the bromine value was 0·4. This treatment had brought about little alteration in the distillation curve. The reaction product was shaken with 98 per cent. sulphuric acid, and 7·6 per cent. by vol. of aromatics were thus found.

In order to prove that the aromatics are not hydrogenated by this treatment, the experiments were repeated after adding 20 per cent. by weight of benzene to the Gyro gasoline. This quantity of benzene was completely recovered in the reaction product.

Upon a direct hydrogenation of the Gyro gasoline with the molybdenum catalyst at 300° C. polymerisation became clearly noticeable, which appears

* To prepare this catalyst nickel-oxide from a nickel nitrate solution is precipitated on kieselguhr with soda. After being washed and dried, the catalyst is reduced in a hydrogen current at about 500° C.

from the distillations of the base material and reaction product given below:

	Base Material.	Reaction Product.
Initial Boiling-point	28° C.	29° C.
10 per cent.	38	44
20	45	51
30	51	58
40	57	65
50	63	72
60	70	79
70	77	87
80	85	101
90	102	184
Final Boiling-point	119	266

Laboratory,
N.V. De Bataafsche Petroleum Maatschappij.

References.

[1] *J.I.P.T.*, 1930, **16**, 73.
[2] Howes, *J.I.P.T.*, 1930, **16**, 54–59.
[3] Ormandy and Craven, *J.S.C.I.*, 1928, **47**, 319r.
[4] *J.S.C.I.*, 1928, **47**, 363r.
[5] The preparation is described in E.P. 331,199, p. 4, lines 65–85. A catalyst of standard activity is obtainable from: 1. International Hydrogenation Engineering and Chemical Co., Carel van Bylandtlaan, The Hague, Holland; 2. Hydro-Engineering Co., 26, Broadway, New York; 3. N.V. de Bataafsche Petroleum Maatschappij, Carel van Bylandtlaan, The Hague, Holland.
[6] *J.S.C.I.*, 1900, **19**, 320; *J.A.C.S.*, 1899, **21**, 1084.

CAUSES OF DETONATION IN PETROL AND DIESEL ENGINES.*

By G. D. Boerlage and W. J. D. van Dyck.

SYNOPSIS.

The combustion phenomena of Diesel and petrol engines are similar in many ways. Self-ignition of the charge in both depends on the interaction of activated oxygen and activated hydrocarbon molecules. "Detonation" may occur in both types of engine, and is due to the vibration of the gases caused by local rapid change of pressure (pink). A "pink" may also be produced by mechanical vibration of the walls due to the high rate of change of pressure. Vibration of other engine parts may produce the "knock." "Rough" or "bumpy running" denotes vibration of heavy engine parts, such as the crank-shaft.

The origin of the various types of detonation must be sought in the engine as well as in the fuel. In spite of the apparent differences between many of the phenomena of combustion, it is hoped to show that there is a close relationship between many of the causes of detonation in both petrol and Diesel engines.

It is commonly assumed that to obtain reasonably smooth combustion it is necessary to compress the air in the case of Diesel engines until the point of auto-ignition of the fuel is reached, and in petrol engines to compress the air–fuel mixture to a point which is only just below that of auto-ignition. At the outset it is necessary to show that these conceptions are inadequate.

Outline of the Process of Combustion in Engines.

Consider first the Diesel engine. If "ignition" is greatly delayed, it is evident that a large quantity of fuel has been injected by the time inflammation starts.

In these circumstances ignition is immediately followed by a heavy explosion of the mixture formed by this quantity of fuel with air, which mixture may be termed "primary gas." Consequently, everything possible should be done to shorten the ignition delay.

In a petrol engine, running without detonation, the flame starts at the sparking plug and progresses smoothly through the air–fuel mixture. If the compression ratio is extremely high, combustion will take place simultaneously and explosively throughout the mixture, even without a spark. At a moderately high compression ratio at which detonation occurs, the flame starts at the plug, and at first moves smoothly through the mixture. The unburnt air–fuel mixture, which may be called the "end gas," is compressed as a result of the advancing flame. If the rate and amount of compression are sufficiently great, the end gas ignites simultaneously

* Abridged version of paper presented on March 6th, 1934, at a Joint Meeting of Various Societies, published in the Journal of the Institution of Automobile Engineers, April 1934.

and explodes, giving detonation (Fig. 1). The compression of the end gas is, to some extent, similar to the compression of the charge by the piston, but it must be remembered that the piston compresses a constant mass of gas and decelerates during the later and more important stage of the process. Compression of the end gas, on the other hand, is effected

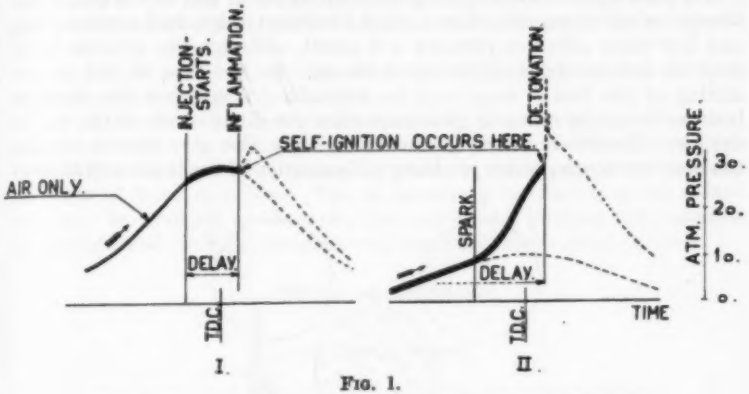

FIG. 1.

SIMILARITY OF SELF-IGNITION IN DETONATING PETROL ENGINES AND IN DIESEL ENGINES.

I. Compression in Diesel Engine.
II. Compression of End Gas in Detonating Petrol Engine.

by an accelerating flame front acting on a gradually diminishing quantity of end gas. It is evident that detonation, or auto-ignition of the end gas, may be avoided by cooling the latter, or even, under favourable conditions, by increasing the speed of travel of the compressing flame, *e.g.* by turbulence, so that the quantity of end gas which explodes is negligible, owing to the fact that the chemical processes leading to detonation in the end gas require time.

DEDUCTIONS FROM THE OUTLINE OF THE COMBUSTION PROCESS.

In the Diesel engine the delay should be short enough to ensure that only a small quantity of primary gas derived from the fuel is present when ignition occurs, as this will avoid knocking. To meet this requirement it is necessary to employ a compression ratio far higher than that needed merely to bring about ignition after a long delay.

In the petrol engine it is necessary to use a compression ratio low enough not only to avoid auto-ignition of the whole charge in the cylinder, but also to avoid auto-ignition of the end gas through an undue amount of compression caused by the advancing flame front.

The degree of mixing of the fuel and air is important for efficient combustion. To denote the degree of atomisation of a Diesel fuel the term "micro-mixture" is proposed, a state of fine atomisation or sub-division corresponding with good micro-mixing. To describe the general distribution of fuel in the charge, the term "macro-mixture" is suggested.

Good and bad macro-mixing mean respectively that the distribution of fuel as a whole in air is complete or incomplete, quite apart from the state of sub-division and drop size of the fuel. Fig. 2 illustrates the possibility of the occurrence of good micro- and bad macro-mixing of the fuel and vice versa.

If a good macro-mixture, *i.e.* good distribution of fuel as a whole in the charge, is not obtained, then a smoky exhaust, high fuel consumption, and low mean effective pressure will result, although the ignition delay may be sufficiently short to avoid knock. In the case of bad macro-mixing of the fuel it may even be advisable to have not too short an ignition delay, in order to give more time for distribution of the fuel in the air. Extremely short ignition delay may also give rise to burning too near the nozzle, which produces carbonisation of the latter and thereby

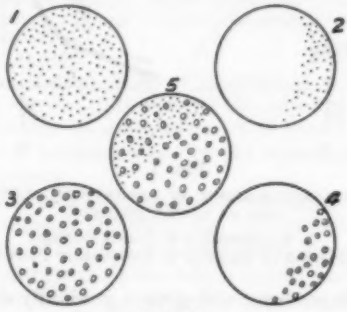

FIG. 2.

1. Good Macro—Good Micro.
2. Bad Macro—Good Micro.
3. Good Macro—Bad Micro.
4. Bad Macro—Bad Micro.
5. Good Macro—Adequate Micro.

a bad macro-mixture. Long ignition delay, apart from causing knock, is objectionable because it allows more time for fuel to condense and cool on the cylinder walls, which again is a bad state of macro-mixture. A high degree of swirl and a separate chamber, as in the "Comet head" engine, may overcome the disadvantages of a very long as well as of a very short ignition delay.

In the petrol engine a small amount of detonation at full load may be an indication that the engine is working quite near the best thermal conditions, and is therefore not always objectionable; it may be added that in this case the engine is working at its Highest Useful Compression Ratio (H.U.C.R.). Heavy detonation, although objectionable, may remove carbon deposits formed in the combustion space under light load conditions. Knock in petrol engines may be diminished by turbulence or swirl, which protects the end gas from excessive compression by the flame; excessive swirl may cause bumpy running.

The Mechanism and Character of Knock.

Knock in engines is due to vibration. Excluding mechanical noises produced by worn and loose parts, vibration is caused by sudden changes in pressure in the burning gases. Changes in gas pressure may bring about vibrations in the gas itself, in the cylinder head and walls, in the piston and its connections, and, when an indicator is used, in the indicator and its parts.

Taking the case of the piston of the indicator, if combustion is rough a diagram such as Fig. 3 is obtained.

The shape of the expansion curve shows that the indicator piston and spring are oscillating owing to some change of pressure. When the engine is running with a less sharp change of pressure, the expansion curve takes the form of the dotted line. This is proved by the fact that the dotted line may be changed to the wavy line merely by striking the indicator piston lightly at the right moment with a suitable mechanical device.

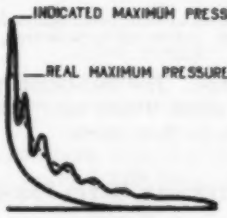

Fig. 3.

KNOCK REGISTERED BY SLOW INDICATOR.

Similar phenomena may occur in the case of the engine piston, but the periods and amplitudes of vibration are, of course, quite different. If, for example, an explosion takes place in the charge when the piston is 90° before top-dead-centre, then torsional vibration of the crankshaft, involving vibrations of connecting rod, piston, etc., may be set up. In this case, and also when the explosion occurs at top-dead-centre in an engine with a very flexible crankshaft, "bumpy running" is the result. With a rigid crankshaft, when the piston is at top-dead-centre, a high rate of change of pressure causes "knock." All combinations of bumpy running and knock may, of course, occur in practice.

The following experiment with a single-cylinder petrol engine illustrates the difference between knock and bumpy running. The engine was coupled to a synchronous electric motor to keep the rotational speed constant. With the engine knocking, the ignition was gradually advanced. The intensity of knocking increased to a maximum, then diminished, and bumpy running set in with further advance in the ignition timing. Knocking eventually ceased, and bumpy running reached a maximum and finally disappeared. When the ignition advance was rather more than 90° early the engine ran quite smoothly with very high maximum pressures. Under these conditions the charge burnt gradually during the compression stroke, the engine being motored by the synchronous motor.

Fig. 4, showing the degree of knock and bumpy running against ignition advance, summarises the results.

The natural period of torsional oscillation of the shaft with the other moving parts of a petrol engine is about 0·01 sec., but the forces required

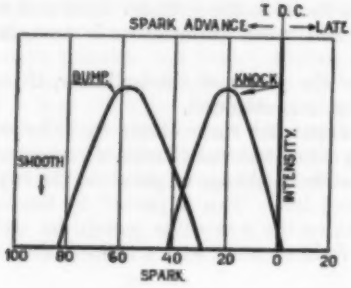

FIG. 4.

KNOCK AND BUMP INTENSITIES.

to set up vibration are large. The oscillation periods of the cylinder walls and of the gases are about 0·0001 sec., but relatively small forces are needed to start vibration in these parts.

CAUSES OF EXTREMELY RAPID PRESSURE RISE.

It has been assumed so far that compression of the charge to beyond auto-ignition would cause simultaneous ignition to take place in all parts of the unburnt gases. Actually, owing to the lack of homogeneity of the charge, ignition probably starts simultaneously at a number of highly activated centres and spreads rapidly from these regions throughout the gases.

Assuming that "true detonation" is an explosive combustion progressing with the velocity of sound (about 2,000 feet per sec. at the temperatures involved), detonating combustion in an engine running at 1,000 r.p.m. would occupy only about 0·0001 sec. Complete combustion of the charge, however, within 0·001 sec. (6° crankshaft angle) might produce a heavy knock. It has been found possible to distinguish in a badly knocking, slow-running Diesel engine, a slight, occasionally high-pitched sound, which was attributed to a sound wave caused by detonation. In this engine the main knock was the usual heavy blow.

What is frequently called detonation is often really only a vibration of engine parts caused by rapid change of pressure, and should be called "knock" or "bumpy running"; the term "detonation" should better be reserved to indicate a high-pitched sound wave set up in the charge.

An experiment made with the C.F.R. variable-compression engine shows that detonation can be produced in a petrol engine without spark ignition. The engine was run at a very high compression ratio, but with the throttle almost closed in order to avoid detonation. When the throttle was opened wide and the ignition simultaneously switched off, detonation

very similar to that obtained with spark ignition was heard. By this method the curves of constant knock intensity in Fig. 5 were determined. A and B represent light and heavy knock respectively, with spark ignition. C represents incipient and D steady knock without spark ignition. Both with and without the spark the noises consist chiefly of a heavy knock,

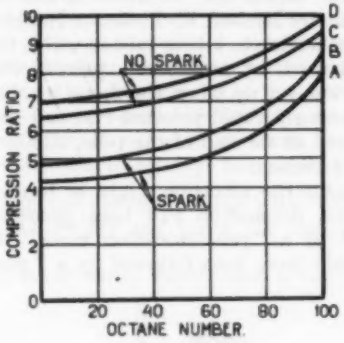

FIG. 5.

CURVES OF EQUAL KNOCK INTENSITY WITH AND WITHOUT SPARK.

but, in favourable circumstances, a high-pitched "pink" can be heard. This pink is "continuous heavy" with the spark and "occasional slight" without the spark. If the C.F.R. is fitted up as a Diesel unit, the noises are practically the same as those obtained when the engine is working as a petrol unit without spark.

PHYSICAL FACTORS WHICH PROMOTE COMBUSTION.

1. *Air–fuel Mixture.*—Good, *i.e.* homogeneous mixing, accelerates combustion, but has less effect on ignition. An over-rich mixture will help ignition, but may hamper complete combustion.

2. *High Temperature* is undesirable in petrol, but is advantageous in Diesel engines, apart from its effect on volumetric efficiency.

3. *Pressure.*—Reduction of air-intake pressure, *i.e.* throttling, increases ignition delay and thereby knock in Diesel engines; and conversely for supercharging. It should be noted that, disregarding the effect of the different proportions of residual exhaust gases, compression temperatures are practically unaffected by throttling and supercharging. On the whole, increase of pressure helps both ignition and combustion, probably owing to the increased concentration of oxygen which it causes.

4. *Spark and Injection Timing.*—The effect of spark setting has been discussed (Fig. 4). In Diesel engines delay increases as injection is retarded and decreases with advance of injection up to a point where it increases again.

5. *Swirl and Turbulence.*—These may, according to their type and function, either accelerate or retard ignition; thus, for example, they may produce a good mixing but strong cooling effect on the cylinder

walls. Movements within the charge generally accelerate combustion. In one engine they may produce good combustion and in another bumpy running. In a petrol engine they may reduce knocking by whirling away the end gas, and in a Diesel engine, by extinguishing the flame, they may promote knocking; each case must be judged individually.

6. *Vibration.*—Like turbulence, vibration of the charge produces mixing. An experiment by Nielsen of Professor Nägel's Laboratory [1] illustrates the effect of vibration in a long tube in which the charge was ignited at one end. He showed, by means of a piezo-electric indicator, that a sound wave which was set up when the flame reached the middle of the tube caused an extremely rapid pressure rise and detonation. A sound-absorbing disk, placed at the end of the tube, eliminated both detonation and the rapid rise of pressure.

In these experiments the vibration might be termed a " pre-detonation wave." If, however, detonation had been produced by a higher gas pressure instead of by a " pre-detonation wave," it is highly probable that detonation might have been followed by a " post-detonation wave."

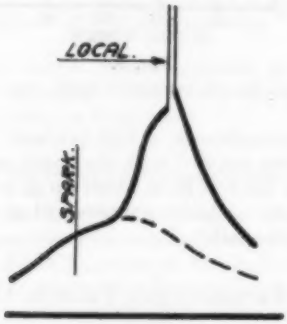

FIG. 6.
PETROL KNOCK.

The latter is shown by the work of Serruys,[2] who obtained diagrams showing high local maximum pressures of about 100 atmospheres [by using a maximum pressure indicator (Fig. 6)]. This post-detonation need not necessarily have the character of a sound wave.

CHEMICAL FACTORS WHICH PROMOTE COMBUSTION.

Although oxidation of hydrocarbons occurs in the presence of air at the temperatures reached during the compression stroke, the rate of reaction even at the maximum temperatures reached is small, except locally at points where the conditions are particularly favourable to oxidation. From such points combustion spreads with great rapidity throughout the whole charge. The delay period in a high-speed Diesel engine may be 0·001 sec., and the time of combustion of the charge about 0·0001 sec., the ignition of the charge proceeding with almost the velocity of sound.

Since the speed of a chemical reaction increases about 100 times for

an increase of 100° C. in the temperature, it can be readily understood that when the temperature at one region of the charge has been appreciably raised by local oxidation, the reaction will spread rapidly in gases already heated as the result of compression.

The reaction between the fuel and oxygen during the delay period differs from that during inflammation only in its relative slowness. The reactions of the delay period only will be studied, since the conditions are relatively simple; as a matter of fact, the concentration of the fuel and air is substantially constant during this period, and thus the reaction speed is governed only by temperature. The temperature of the mixture just before the inflammation is about 550–700° C. Accurate measurement of this temperature is difficult owing to its short duration. It is, however, proposed by the Authors to attempt to measure it:

(*a*) by determining the electrical breakdown voltage in the gases, from which the density and hence the temperature can be calculated; or

(*b*) by measuring the intensity distribution in the ultra-violet absorption bands.

Active Oxygen and Oxygen Concentration.

Since at 600° C. and a compression ratio of 9:1 any hydrocarbon molecule in the charge collides more than one million times in 0·0001 sec. with oxygen molecules, it is evident that mere collision is not sufficient for combustion, and the Authors therefore suggest that the molecules must be "activated" before reaction can take place. The presence of substances which produce active oxygen, such as ozone, ethyl nitrate, and peroxides, is known to shorten ignition delay. The fact that peroxides assist ignition does not imply that peroxides and similar compounds are the chief or necessary cause of knock owing to their formation in the charge. The chemically known peroxides, owing to their instability, are unlikely to be formed at the high temperature and in the short time in which a Diesel fuel is brought to a high temperature after injection into the engine. Since Dumanois [3] has shown that there is a good correlation between the heptane number (= 100 minus octane number) of a fuel in a petrol engine and its cetene number determined in a Diesel engine, it seems that auto-ignition is generally similar in the two types of engine; therefore, peroxide formation during the compression stroke is probably not the usual cause of detonation in petrol engines. Further evidence has been obtained by the Authors, who have found that cetene values obtained by measuring ignition delay in the petrol engine test without spark ignition agree fairly well with those determined in Diesel engines.

The influence of the oxygen concentration [4] is proved by the results of Fig. 7, which shows that ignition delay is shortened, or reaction speed increased, by increasing the total oxygen concentration in the air. The curves show that with good accuracy this connection is hyperbolic, *i.e.* the reaction speed is proportional to the oxygen concentration. Similarly, ignition delay is increased by throttling and reduced by supercharging a Diesel engine, and the effect is due, not to the pressure as such,

but to the variation in oxygen concentration in mol./c.c. which it produces. Further, it is concluded that the delay in ignition due to the necessity for the fuel to warm up is in normal cases negligible compared with the delay due to slow reaction speed.

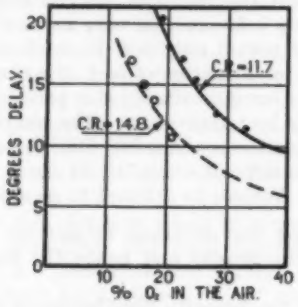

FIG. 7.

IGNITION DELAY AS A FUNCTION OF OXYGEN CONCENTRATION.

ACTIVE HYDROCARBONS.

At temperatures of 550–700° C. most hydrocarbons are unstable and decompose or crack. It would seem, therefore, that the thermal stability of a fuel probably has an important effect on its behaviour in the engine. This point was put forward many years ago by Rieppel.[5] To investigate

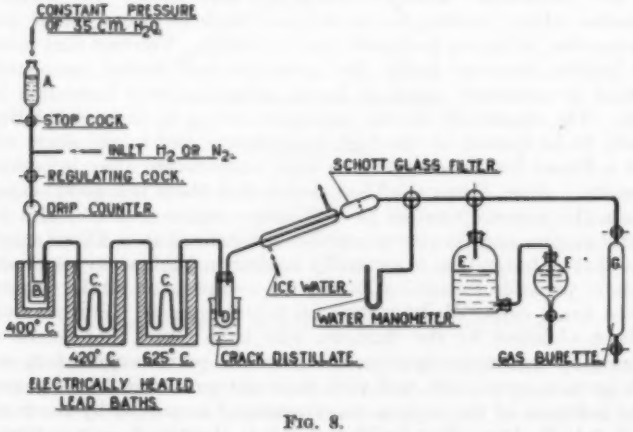

FIG. 8.

APPARATUS FOR THE DETERMINATION OF THE THERMO-STABILITY OF HYDROCARBONS.

the question the Authors have measured the "initial cracking speeds" of fuels at known temperatures in an apparatus shown diagrammatically in Fig. 8. The oil is fed by drops at a regular rate into vessel B, in which it evaporates. The vapour passes into apparatus C, in which cracking

takes place. The higher boiling and the unchanged products are collected in D and the gases in the burette G, in which they are measured. Fuel fractions of narrow boiling range were first tested in this way and the amount of cracking was determined by fractional distillation and measurement of the amount of material distilling outside the boiling range of the original fuel. The first results were mentioned at an I.P.T. discussion in 1932.[6] In later work the average molecular weight of the liquid fuel was measured by the Victor Meyer method before and after cracking, the molecular weight of the gases formed by cracking being measured by combustion analyses. From these data calculations of the increase in the number of molecules due to cracking were made. Considerable experimental difficulties had to be overcome in this work, *e.g.* in controlling and measuring the important factors of temperature and time of cracking. The influence of the material of the cracking tube had also to be con-

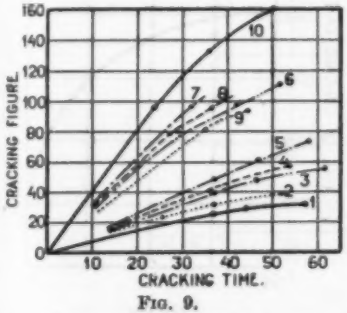

FIG. 9.

RELATION BETWEEN CRACKING FIGURES AND CRACKING TIME.

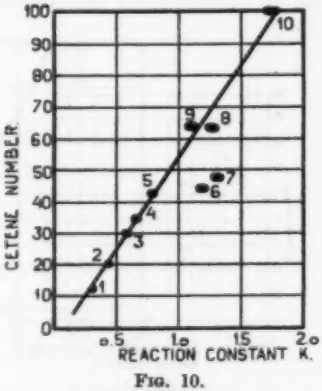

FIG. 10.

REACTION CONSTANT K AGAINST CETENE NO. CRACKING TEMP. 635° C.

sidered, and ultimately two special Krupp chromium steels, NCT_3 and FK 345, of high resistance to heat and corrosion, were used, since they showed negligible catalytic action. Very careful cleaning of the cracking tube was necessary before each experiment, and the apparatus was purged out with oxygen-free nitrogen.

Results for various fuels showing the linear relationship between time and amount of cracking for initial cracking at 635° C. are given in Fig. 9.

The maximum time of cracking was about $1\frac{1}{3}$ sec. From results of this type the reaction constant "K" was derived for Diesel fuels of different sources, and in Fig. 10 the values of "K" are plotted against the cetene number of the fuels, each fuel being represented by an "error ellipse."

Although the correlation between the two properties is evident, no explanation of the anomalous behaviour of fuels 6 and 7 has yet been found.

The effect of temperature on the rate of initial cracking was investi-

gated, and it was found that a rise of 10° C. increased the cracking speed to about 1·3 times the original rate.

In the gasoline range it is known that the thermal stability and anti-knock value of the constituent hydrocarbons increase as the boiling-points fall. Cracked gasolines, which have, of course, been kept at high temperatures for very long periods compared with those of the phases of an engine cycle, generally have higher anti-knock value than straight-run gasolines of the same origin and volatility. Determination of the initial cracking speeds of gasolines showed that the temperature effect was greater than for Diesel fuels, a rise of 10° C. increasing the rate to about 1·5 times the original. This factor varied somewhat with different gasolines and also with the temperature. The reaction constants "K" for the initial rate of cracking of a number of gasolines are shown in Fig. 11 plotted against the octane numbers of the fuels. Normal heptane, fuel No. 6, falls on the curve, but *iso*-octane, No. 7, has an abnormally

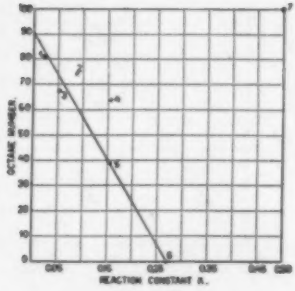

FIG. 11.

REACTION CONSTANT K AGAINST OCTANE NO. CRACKING TEMP. 625° C.

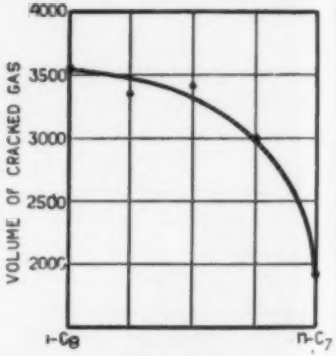

FIG. 12.

VOLUME OF CRACKED GAS FOR MIXTURES OF I-C_8 AND N-C_7.

high cracking speed. Since the temperature coefficient for cracking speed of *iso*-octane is practically the same as that of normal heptane in the range 570–650° C., mixtures of the two substances were examined. The results are plotted in Fig. 12, which shows that something abnormal occurs in the initial cracking of the mixtures, since gas formation does not vary linearly with composition.

The anomalous behaviour on cracking of *iso*-octane, which, in accordance with its compact molecular structure,[7] shows a higher anti-knock value than *n*-heptane, suggests that thermal instability is not the only requirement for rapid reaction between a fuel and oxygen. The products of cracking probably differ considerably, according to their structure, in their rates of reaction with activated oxygen. For example, *iso*-octane may split by cracking into *iso*butyl radicals which are symmetrical in configuration like triphenylmethane, and probably relatively stable against further decomposition or oxidation. In this connection it has been found that *tetra-iso*butylene, which might be expected to decompose

in a similar manner to *iso*-octane, also resembles the latter in its rapidity of cracking and relatively poor ignition quality in a Diesel engine. No substances having a low cracking speed and high oxidation rate have yet been found.

The mechanism of the reaction between oxygen and the hydrocarbon fragments formed by cracking of the fuel is not known, but spectroscopic analysis of the absorption and emission bands during cracking and oxidation may throw light on the subject. Some work on the oxidation of methane in a flame has already been done by Lauer.[8]

The concentration of active hydrocarbons formed by cracking of the fuel must have as great an influence as the concentration of active oxygen on the rate of reaction. In the petrol engine the effect of mixture strength, on which depends the concentration of active hydrocarbons, can be studied by running at high compression ratios without spark ignition. In the Diesel engine the fuel vaporises and the vapour reaches the air temperature in an extremely short time. These conclusions are supported by the

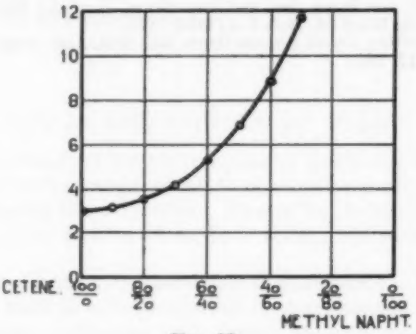

FIG. 13.

IGNITION DELAY OF CETENE-1-METHYLNAPHTHALENE BLENDS.

observation that only hydrocarbons with very high boiling-points of 400–500° C. give ignition delays longer than would be expected from the behaviour of fuels of similar chemical nature but lower boiling-point. Further, strong pre-heating of fuels before injection has a negligible effect on ignition delay.

The influence of fuel concentration on ignition delay can be properly studied only when the delay is longer than the injection period, owing to the uncertainty of the average fuel concentration when the delay is shorter than the injection period. In the discussion of a paper [9] Bird explained anomalies in ignition lag by differences in fuel concentration, a fall in the air–fuel ratio from 10 to 3 : 1, reducing the delay from 0·016 to 0·004 sec.

In mixtures the concentration of active hydrocarbons is approximately the sum of the partial concentrations of the active components, but if one of the constituents is unable to produce active substances under the prevailing temperature conditions, it may, in Duff's [10] nomenclature, be termed a diluent. This is illustrated in Fig. 13, which gives a delay

curve for cetene and methylnaphthalene blends, showing that the delay is approximately inversely proportional to the concentration of cetene, the other constituent being an inert diluent.

This paper is published by kind permission of the Directors of the Bataafsche Petroleum Maatschappij. Thanks are also due to the staffs of the "Proefstation Delft," to the Company's Amsterdam Laboratory, and especially to Mr. Broeze, for their collaboration and assistance.

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THE PRACTICAL TESTING OF A CONTINUOUS PETROLEUM STILL.*

By A. H. Goodliffe, B.A., B.Sc.

The object of this paper is twofold: to indicate (*a*) the theory and practice of the normal method of testing distilling equipment when first received from the manufacturers; (*b*) the results obtained in practice on the various details of the plant to assist designers in their efforts to produce an economical apparatus from the point of view of both capital expenditure and operating cost.

The paper is divided into three parts :—

I. Description of plant.
II. Log of run and balances.
III. Calculations on plant and equipment.

Part I.—DESCRIPTION OF PLANT.

The plant was designed for the purpose of producing white spirit and spirits with close boiling ranges of 20° C. or more from the lighter fractions of a variety of roughly topped crudes. Except for the heating steam, which is raised in a central station of modern design, the plant is completely self-contained.

Dealing first of all with the general flow of materials, the crude is pumped from its storage tank to a residue/crude heat exchanger, from there to a product/crude heat exchanger and thence through two steam heated preheaters. Some distillation steam is injected into crude spirit at its point of entry into the first of the two preheaters.

The liquid and vapour issuing from the second preheater are now taken through a 4-in. line to the first of two columns, which, except for minor details, are similar in design. In the first, alternative feed supply to four plates is provided (the eleventh, thirteenth, fifteenth, and seventeenth counting from the top). With the type of crude at present under discussion, the feed was taken on to the highest plate (No. 11). The liquids fall over the trays to the twenty-second tray (the lowest) and thence to the bottom of the column. Some of this liquid is recirculated by means of a centrifugal pump to the twentieth tray through a steam-heated reboiler or reheater, and again falls to the bottom of the column. The residue is pumped intermittently to storage *via* the first heat exchanger. To assist in the evaporation of the spirit, further live steam is injected into the bottom of the column above the liquid level through a steam "spider" (a pipe drilled with small radial holes staggered along the upper surface).

The vapours pass upwards through bubble caps into the top of the

* Abridged version of paper read at a joint meeting with the Institution of Chemical Engineers on March 21st, 1934.

column, whence they are taken through a vapour pipe and returned to the head of the column and away by means of another vapour line to the bottom of the second column. A reflux condenser can be placed, if necessary, on the head of the column, but experiments have shown that with the rather limited amount of heat available when employing steam heating, any reflux required is more suitably supplied by means of liquid from the bottom of No. 2 column.

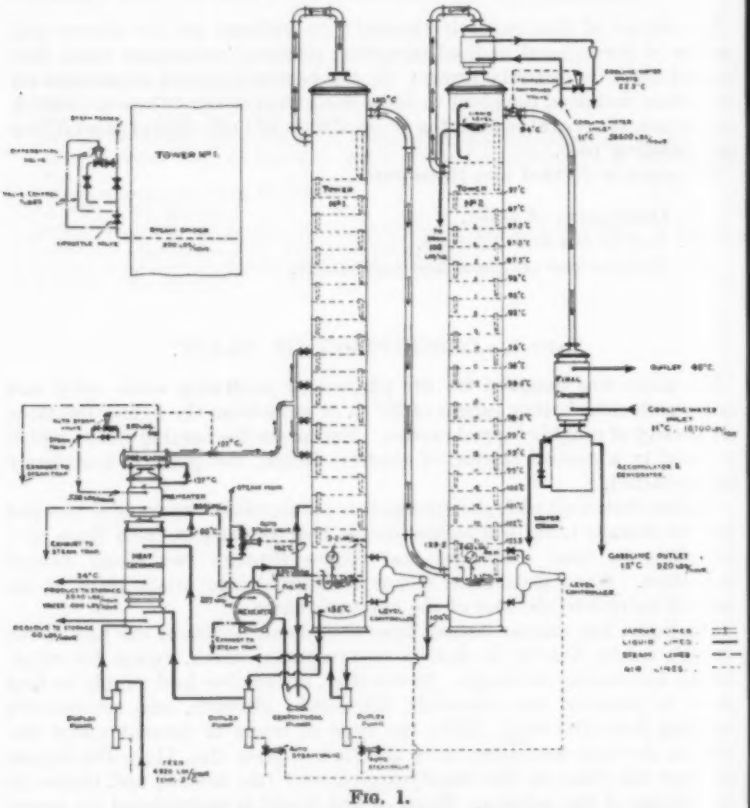

FIG. 1.

CONTINUOUS PETROLEUM STILL. FLOW DIAGRAM.

The vapour inlet to the second column is situated below the bottom (twenty-second) tray, but above the liquid level. A process steam coil is provided in the same manner as in the first column. The product (the material for which the distillation is undertaken) is pumped away from the bottom of the tower continuously. The vapours rise through the column, and are taken out by a vapour line on to the top of a water-cooled reflux condenser. The vapours, both steam and spirit, are partially condensed, and fall back concurrently with the balance of the vapours into

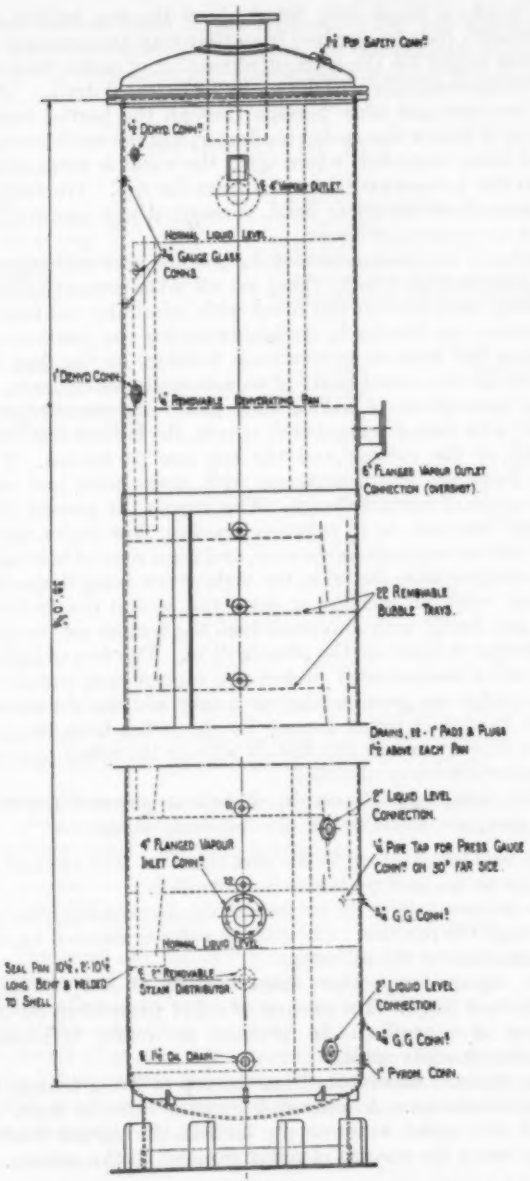
¾" Pop Safety Conn.
½" Drip'd Conn.
6" Vapour Outlet
Normal Liquid Level
½" Gauge Glass Conns.
1" Drip'd Conn.
½" Removable Deviating Pan
6" Flanged Vapour Outlet Connection (overshot)
22 Removable Bubble Trays.
Drains, 22 - 1" Pads & Plugs 1½" above each Pan
2" Liquid Level Connection.
4" Flanged Vapour Inlet Conn.
½" Pipe Tap for Press Gauge Conn. on 30° far side.
½" G.G. Conn.
Normal Liquid Level
6" Removable Steam Distributor
Seal Pan 10'-4", 2'-10½" long Bent & welded to Shell
2" Liquid Level Connection.
½" G.G. Conn.
½" Dr. Drain
1" Pyrom. Conn.

FIG. 2.

NO. 2 COLUMN—CONTINUOUS PETROLEUM STILL.

the reflux head—a blank tray fitted above the top bubble tray. The reflux downtakes (two in number) from that tray are arranged to provide a large liquid height for the efficient separation of water from the spirit: the water is automatically withdrawn by an external drain. The vapours remaining uncondensed after passage through the partial condenser are led to the top of final water-cooled condenser, and the condensate gravitates to the final water separator, where again the water is automatically withdrawn from the bottom and the spirit from the top. The former, bulked with the water from the reflux head, is removed to a common sump, and the latter to a rundown receiver.

A clear idea of the construction of the heaters, heat exchangers and condensers is given in Figs. 4 to 8. They are all of the counter-current tubular type of welded construction and fitted with Admiralty mixture tubes.

Both columns are similar in design, excepting the position and size of the inlet line, the bottoms recirculation facilities on the first tower, and the provision on the second tower of an automatic water drain. They are constructed throughout of welded steel plates and buttstraps, and each end is fitted with dished pressed steel covers, the bottom one being welded to the sides of the column and the top one to flanges. Twenty-two removable trays are fitted, complete with drain holes and bubble caps and reflux pipes of normal design. The vapour, in passing through the bubble caps, does not, as in common practice, flow under the periphery of the cap, but the cap rests on the tray, and three rows of holes are punched at different heights from the edge, the highest row being designed for small throughputs; with an increase in duty the second row is brought into operation, and finally with maximum load the bottom set functions. The minimum height of liquid on the plate is $2\frac{1}{2}$ in. The flow of liquid is across the plate, and a thermometer pocket and tapped boss, normally plugged for sample cocks, are provided for each tray midway round the circumference. A fixed weir forms a sump for the reflux from the tray above, and ensures that no vapour can find its way up the reflux pipe or interfere with the smooth delivery of reflux.

Automatic temperature controls, of vapour pressure (ether) and air-operated types, are installed for the following duties:—

1. The feed temperature to the first column. The amount of heating steam to the last preheater is controlled.
2. The temperature of the bottoms of the first column after circulation through the reboiler. The control valve is situated on the heating steam inlet to the reheater.
3. The vapour temperature from the top of No. 1 column to the bottom of No. 2. The amount of reflux pumped up by the product pump is controlled. In practice no reflux is required when producing white spirits.
4. The vapour temperature from the top of No. 2 column before the final condenser. A controlled by-pass valve is fitted across the inlet and outlet water-supply lines to the partial condenser, and this varies the amount of reflux supplied to the column.

The liquid level controllers, regulating the amount of steam to the relevant pumps, are fitted to the bottom of both columns.

The steam spiders, fitted in the bottoms of the two towers, are each fitted with a pressure-controlled by-pass, for the purpose of guaranteeing an invariable rate of steam supply independent of steam pressure variation.

PART II.—LOG OF RUN.

Plant started	9 a.m., 12.12.1933.
Date of trial	9·0–17·30, 13.12.1933.
Mean temperature on day of trial	2° C. (shaded).
Wind on day of trial	E. to N.E. Gale force.
Pressure on day of trial	29·86 rising slowly.
Material processed	Venezuelan Crude White Spirit.
Product required	White Spirit Flash Point (Abel), 98° F.

Specification.

Material.	Crude.	Product required (White Spirit).
Sp. Gr. 60/60° F.	0·783	—
Flash Point (Abel)	—	98° F.
Distillation A.S.T.M.	°C.	°C.
I.B.P.	148	155
10%	153	—
20%	156	—
30%	158	—
40%	160	—
50%	162	—
60%	165	—
70%	168	—
80%	172	—
90%	179	—
F.B.P.	198	192
Recovery	99·5%	—

The efficiency of distillation must be such that "gaps" occur:—

1. Between the I.B.P. of residue and F.B.P. of product.
2. Between the I.B.P. of product and F.B.P. of tops.

The averages given are calculated only on the dips taken previous to 12·30. The abstraction of materials on the trays for samples rendered the readings taken after that time inaccurate.

Rate of crude feed	628 gals. at 15° C.
Specific gravity	0·782.
Rate of crude feed to plant	4920 lb. per hr. . . (1)

Residue.—The small amount of "bottoms" made in the bottom of the first column precluded its being pumped away continuously.

The level was allowed to build up to a certain height, and then liquid was slowly pumped away till it had fallen again; the time of the test was too short to permit of an accurate estimation of the amount produced, but measurements taken over a large number of similar runs show that an amount of 0·85 per cent. of crude by weight is made, and this figure is taken in the subsequent calculations.

Rate of residue production = 40 lb. per hour . . . . . (2)

Product.—The conditions of operation were such that a relatively large percentage of steam had to be injected into the first column. The tem-

peratures in the second column were low enough to cause some condensation on the plates of the column which, falling back into the bottom, was pumped away with the spirit.

Time.	10·0.	11·0.	12·0.	14·0.	14·40.	17·30.	Remarks.
Mains steam press.: lb. per sq. in. gauge .	146	128	140	135	135	155	—
Ditto, Temp. °C. .	205	208	205	195	197	198	—
Live steam meter .	726,230	727,650	728,450	731,005	731,984	730,820	—
Actual time of reading meter . .	10·5	11·13	11·50	14·00	14·40	17·46	—
Condensate ex first preheater . .	2′ 02″	2′ 28″	2′ 14″	—	2′ 16″	—	Time to fill 2-gallon container.
Ditto, second preheater . . .	4′ 45″	4′ 55″	4′ 50″	—	4′ 40″	—	Ditto.
Ditto, reheater. .	6′ 00″	5′ 43″	5′ 50″	—	5′ 40″	—	Ditto.
Ditto, final condenser	1′ 28″	1′ 24″	1′23·5″	—	1′ 25″	—	Ditto.
Temp. of crude to plant °C. . .	5	5	5	4	4	4	—
Temp. intermediate between preheaters °C. . . .	140	137	137	140	138	140	—
Temp. of inlet to No. 1 column °C. .	136	136	137	136	136	137	—
Temp. of bottoms of No. 1 column °C. .	143	157	155	135*	141	160	*Steam trap became water logged.
Temp. of reheater to No. 1 column °C. .	153	165	162	139*	148	166	—
Temp. of vapour to No. 2 column °C. .	122	132	129·5	120	124	122	—
Temp. of bottoms of No. 2 column °C. .	104	103·5	104	104	105	105	—
Temp. of vapours to partial condenser °C.	97	97·2	97	96	95·5	96	—
Temp. of vapours to final condenser °C.	94	94·2	94	93	92	94	—
Temp. of product from heat exchangers °C.	34	34	34	34	36	36	—
Temp. of benzine from final condenser °C.	13	12	13	13	14	14	—
Temp. of water to partial condenser °C. .	10	10	11	11	10	11	—
Temp. of water from partial condenser °C.	21·5	21·0	21·5	21·0	21·5	22·0	—
Pressure bottom column No. 1 lb. per sq. in. . . .	3·35	3·3	3·3	3·5	3·7	3·7	Slight variation.
Ditto, No. 2 . .	2·5	2·4	2·65	2·65	2·75	2·80	Very slight variation.

An estimation of the amount of water is easily arrived at by using a water-finding paper on the end of the dipstick when tank dipping, and the volume of spirit determined by dip in the normal way.

Production of condensed steam . . . 40 gals. per hour.
= 400 lb. per hour . . . (3)

Production of white spirit . . . . 502 gals. per hour at 15° C.
Specific gravity, 60/60° F. . . . . 0·7855.
Rate of manufacture . . . . . 3940 lb. per hour . . (4)

Log of Materials.

Time.	9·30.	10·30.	11·30.	12·30.	13·30.	14·30.	15·30.	16·0.
Dip of feed tank	5′ 6·2″	5′ 1·7″	4′ 9·3″	4′ 4·8″	4′ 0·4″	3′ 8″	3′ 3·8″	—
Temp. °C. feed tank	6·0	5·0	5·0	5·0	4·0	4·0	4·0	—
Dip of product tank	0′ 3·8″	0′ 11·3″	1′ 5·4″	1′ 10·3″	2′ 2·9″	2′ 7·0″	2′ 10·3″	—
Water dip product tank	2·6″	3·5″	4·4″	5·0″	5·7″	6·3″	6·8″	—
Temp. °C.	22·0	22·0	22·0	22·0	22·0	21·0	21·0	—
Dip of residue tank	1′ 5·8″	1′ 5·8″	1′ 5·8″	1′ 5·8″	1′ 5·8″	1′ 5·9″	1′ 6·0″	—
Water dip residue tank	4·6″	4·6″	4·6″	4·6″	4·6″	4·6″	4·6″	—
Temp. °C residue tank	12°	12°	12°	12°	12°	12°	12°	—
Dip of tops tank	2′ 11·5″	3′ 0·2″	3′ 1·2″	3′ 2·0″	3′ 2·9″	3′ 3·6″	3′ 4·3″	—
Water dip of tank	0·0	0·0	0·0	0·0	0·0	0·0	0·0	—
Temp. °C. dip tank	6°	6°	6°	6°	6°	6°	6°	—

Balance of Materials.

(All Volumes in Gallons.)

Time.	9·30.	10·30.	11·30.	12·30.	13·30.	14·30.	15·30.	Average.
Vol. in feed tank	7651	7032	6418	5786	5170	4558	3974	—
Rate of feed of crude	—	619	614	632	616	622	582	621
Temp. of crude tank °C.	—	5	5	5	4	4	4	5
Corrected rate of feed.	—	626	621	639	623	629	588	628
Vol. of water and white spirit in tank	126	672	1246	1777	2314	2825	3252	—
Vol. of water alone in tank	75	118	164	198	240	275	312	—
Vol. of product alone in tank	51	554	1082	1579	2074	2550	2940	—
Production of white spirit	—	475	528	497	495	476	398	500
Production of water	—	43	46	34	42	35	38	40
Temp. of tank °C.	22	22	22	22	22	22	22	22
Corrected production of white spirit	—	477	530	500	497	474	396	502
Vol. of residue and water	1288	1288	1288	1288	1288	1298	1308	—
Vol. of water alone	175	175	175	175	175	175	175	—
Vol. of residue alone	1113	1113	1113	1113	1113	1123	1133	—
Production of residue	0	0	0	0	0	10	10	—
Temp. of tank °C.	12	12	12	12	12	12	12	—
Corrected production of residue	—	—	—	—	—	10	10	—
Vol. of water and tops in tank	3389	3502	3635	3742	3863	3957	4025	—
Vol. of water alone	Nil	Nil	Nil	Nil	Nil	Nil	Nil	—
Production of tops	—	113	132	107	121	104	95	118
Temp. of tank °C.	6	6	6	6	5	5	5	6
Corrected production	—	115	134	108	122	105	96	119

Tops.—Although a water bottom was present in the tank, efficient separation was maintained in the water separator situated after the final condenser, so that no increase in water was measured throughout the run.

Production of tops (spirit) . . . . . 119 gals. per hour at 15° C.
Specific gravity at 60/60° F. . . . . 0·7715.
Rate of manufacture . . . . . 920 lb. per hour . . . (5)

Balance.—From :

	lb./hour.		lb.
(1) Crude feed . . .	4920	(2) Residue	40
		(4) White spirit . . .	3940
		(5) Tops	920
			4900
		Loss (0·4%) . . .	20
			4920

It is perhaps fortunate that the balance resolved itself so well. In runs of long duration figures are obtained very similar to these throughputs and the loss is of the same order.

A check of doubtful value on the throughput may be obtained by considering the feed pump. This is a steam-driven duplex pump, the steam supply pressure of which is kept constant by a reducing valve, in order that when the shut-off valve is opened a predetermined amount, variations in the main steam supply will not affect the speed of the pump. It might, therefore, be classified as a meter. Although the feed-tank level was somewhat above the centre line of this pump (so that there was actually a slight pressure on the suction side), the delivery pressure oscillated about a mean figure of 35 lb./sq. in., and this comparatively large pressure drop militates against accuracy. However, the particulars are as follows :—

Duplex pump.	4½ in. by 3¾ in. by 4 in.
Speed of pump	35 double strokes per minute.
Capacity of pump	669 gals. per hour at 5° C.
	= 677 gals. per hour at 15° C.

From (1) the volume of feed = 628 gals. per hour.

Balance of Live Steam Consumption.—The process, distillation or live steam injected both into the tubes of No. 1 preheater and the bottom of No. 1 column are abstracted in three places. A portion, already calculated (cf. 3), is pumped away with the white spirit product, a small amount from the automatic water separator at the top of No. 2 column, and the rest from the dehydrator, or water separator situated immediately below the final condenser.

The total live steam was measured by a rotary meter, which, as it had been overhauled by the makers, should give an accuracy of $\pm$ about ½ per cent. for non-fluctuating loads similar to the present. (Actually the meter was calibrated with saturated steam at 125 lb./sq. in., and the correction necessary for steam at 140 lb./sq. in. gauge and 250° C. temperature is 1·016, and is neglected.)

With regard to the division of the live steam to the two points of usage, no method for separate measurement was available while the plant was in operation. A test was undertaken before the plant was on grade by cutting out first of all the steam to the preheater for a quarter of an hour, and then opening that to the normal amount and closing the supply to the column, the readings of the meter being taken in each case. The addition of these two separate readings conform well to the average for the period, but as such a test tends to flood the column trays with water, delaying the time when satisfactory fractionation commences, no further trials were attempted.

Dealing now with the allocation of condensed water between the water drain in the reflux head of the second column and the final benzine–water separator, again no facilities are available for a continuous analysis while the plant is on grade. The two outlet pipes are taken into a common waste pipe, the total volume of which can be, and was, determined by means of a 2-gal. measure, the times taken being entered in the log of the run under the heading "Condensate from Final Condenser." However, the down-pipe from reflux-head water-drain was emptied into a funnel at a low level (to prevent the water syphoning into the final condenser water separator). A temporary flexible hose was connected to the open end, and the 2-gal. measure employed as before. The method proved unsatisfactory, as the supply was somewhat periodic, and different times were secured. At any rate, the amount is small compared with the amount of reflux.

No convenient method of measuring the amount of water in the final separator was evolved; various ideas presented themselves, but were discarded as unreliable.

Relevant Extract from Log Sheet.

Time.	Live Steam Meter.	Consumption of Live Steam in lb.		Condensate ex Final Condenser Time to fill 2-gal. measure.	Condensate ex Final Condenser lb. per hr.
		Actual.	Per Hr.		
10·5	726,230	—	—	88·0 secs.	820
11·13	727,650	1420	1290	84·0 ,,	860
11·50	728,450	800	1300	83·5 ,,	863
14·00	731,005	2545	1180	—	—
14·40	731,984	979	1320	85·0 ,,	850
17·46	735,820	3936	1270	—	—
Mean	—	—	1250	—	850

Measurement of Individual Sources of Live Steam Consumption on 12.12.1933.

No. 1 *preheater.*

At 10 hr. 16 min. 5 sec., the meter reading was 600,200.
At 10 hr. 31 min. 5 sec., the meter reading was 600,412.
Mains steam pressure and temp. 147 lb. per sq. in gauge and 201° C. respectively. (Meter correction, 1·016.)
Hence steam consumption in preheater alone = 850 lb./hr.

No. 1 *column.*

At 10 hr. 45 min., the meter reading was 600,693.
At 11 hr. 0 min., the meter reading was 600,786.
Steam conditions as above.
Steam consumption on No. 1 column alone = 380 lb. per hr.
∴ Total live steam used = 1230 lb. per hr.

For the purpose of subsequent calculations, the direct meter reading of 1250 lb. per hour obtained from the log sheets will be used, and it is safe to assume that relative consumption of the two points of usage will not vary.

Hence live steam in preheater . . . 860 lb. per hour . . (6)
Hence live steam in No. 1 column . . . 390 lb. per hour . . (7)

Allocation of Condensed Live Steam.—The mean weight of live steam condensed by the partial and final condenser together has already been computed at 850 lb. per hour.

In taking measurements of the amount of water from the reflux head, five tests were made, spread over 12.12.1933, the time in minutes and seconds required to fill a 2-gal. container being as follows:—

10′ 00″; 12′ 20″; 11′ 25″; 11′ 12″; 12′ 25″

From which the following rates are obtained:—

lb. per hour.

120; 97·2; 103; 107; 96·5

Mean rate of water ex reflux head . . = 106 lb. per hour . . . (8)

Hence by difference the weight of live steam condensed in the final condenser . . = 744 lb. per hour . . . (9)

Steam Consumption in Heaters.

First preheater :— Time.	10·00.	11·00.	12·00.	14·00.	14·40.	17·30.	Average.
Time to fill 2-gal. measure	2′ 02″	2′ 28″	2′ 14″	—	2′ 16″	—	—
Amount of steam condensed lb. per hour .	600	486	538	—	530	—	538
Second preheater :—							
Time to fill 2-gal. measure	4′ 45″	4′ 58″	4′ 50″	—	4′ 40″	—	—
Amount of steam condensed lb. per hour .	253	242	248	—	257	—	250
Reheater :—							
Time to fill 2-gal. measure	6′ 00″	5′ 43″	5′ 50″	—	5′ 40″	—	—
Amount of steam condensed lb. per hour .	200	210	206	—	212	—	207

Hence heating steam used in first preheater . 538 lb. per hour . . . (10)
Hence heating steam used in second preheater . 250 lb. per hour. . . . (11)
Hence heating steam used in reheater . . 207 lb. per hour. . . . (12)

The outlets of the steam from each heater were closed by a steam trap, the functioning of which was satisfactory, except for the reheater, which once during the course of the test was found to be water-logged, producing the low temperatures noted at 14·00 o'clock.

It will be noticed that the average steam usage in each heater conforms well with those noted at 12·00. In arriving at the amount of heat absorbed by the heaters, the steam temperature and pressure will be taken as those existent at that time.

The temperature of the condensed water from the heaters will be taken as that for saturated steam at 140 lb. per sq. in. gauge, and it must be assumed that no steam was allowed to escape past the steam traps. The waste line was taken some 50 ft. through a culvert to a common sump. To avoid the loss of water consequent on the reduction of pressure from 140 lb. per sq. in. to atmospheric, the culvert was kept full of water. The amount of steam issuing from the two preheater lines was extremely small; that from the reheater is not considered, although the volume was quite impressive, and due to this a small amount of splashing occurred as the level in the 2-gall. container approached the top.

(Steam tables used throughout—based on Callendar's values.)

	B.Th.U. per lb.	
Latent heat and sensible heat of superheat . . =	890	
	B.Th.U. per hour.	
Heat absorbed in first preheater (cf. 10) . . =	478,000 . .	(13)
Heat absorbed in second preheater (cf. 11) . . =	222,000 . .	(14)
Heat absorbed in reheater (cf. 12) . . . =	184,000 . .	(15)

Cooling Water.—No direct measurements of the cooling water to the two condensers, the partial condenser on the top of No. 2 column, or the final condenser, were possible, and the large volume precluded the consideration of measures. The method adopted was to inject into the suction of the centrifugal pump a few crystals of potassium permanganate, and to note the time taken for the colour to travel to the outlet of the partial condenser, where the water was led into a funnel (to prevent vapour-locking in the condenser). This was repeated with the shut-off valve to the final condenser temporarily closed. The delivery pressure on the centrifugal pump was noted in each case. The length and diameter of delivery lines were measured.

Hourly readings were not taken of these temperatures and pressures; spot readings taken as opportunity offered showed very concordant results, as the pump pressure varied only within a small amount.

Reference to the pump manufacturers, who were supplied with full information, elicited a capacity quite well in accordance with the computed figures. The experimental figures are taken in the succeeding calculations.

When taking the time for the water to traverse the intervening length of line, there was no doubt as to when it began to change colour; there was a clear line of demarcation between the "water-white" and the colour, and the only experimental error may be attributed to the personal error in starting and stopping the watch at the correct moment. This should not be more than $\pm \frac{1}{2}$ second, and indeed all the times for the same pressure fall within this amount. After the first change of colour, the same depth continued for 7½–11 seconds (depending probably on the amount of crystals injected) and then fairly quickly died away.

Straight-through cocks with graduated pointer were the only means of shutting the water off, the increase in velocity or drop in pressure through them were comparatively slight, as they are maintained full open during operation.

The data are as follows:—

	lb. per. sq. in. gauge.
Pressure when both partial condenser and final condenser in parallel .	29·2
Pressure when partial condenser only is used	32·5
Length of 4-in. main to common tapping-off point	84 ft.
	Down to funnel.
Length of 3-in. riser line to partial condenser	43 ft. + 2 ft.
Length of 3-in. riser line to final condenser	20 ft.
Length of 3-in. horizontal line to final condenser	10 ft.
Time for water to flow from pump to outlet of partial condenser when both condensers are open	34 secs.
When only partial condenser is open	29 secs.

Let M = mass of water in lb. per second passing through partial condenser when final condenser is shut off.

Then time for water to pass through condenser:

$$= \frac{62{\cdot}3}{M} \times \frac{16 \times 13{\cdot}8}{144} \text{ (neglecting end effects).}$$

And $$\frac{62{\cdot}3}{M \times 144}(12{\cdot}56 \times 84 + 7{\cdot}07 \times 45 + 16 \times 13{\cdot}8) = 29{\cdot}0.$$

Whence $M = 23{\cdot}8$ lb. per second.

Assuming that for small differences of pressure the velocity is proportional to (pressure difference)$^{\frac{1}{2}}$, the flow being turbulent.

When both partial and final condensers are open, total amount of water used $= 23{\cdot}8 \times \sqrt{\frac{11{\cdot}0}{14{\cdot}3}} = 20{\cdot}9$ lb. per second. $\frac{11{\cdot}0}{14{\cdot}3}$ because 18·2 lb. per sq. in. is the static head due to the height of the outlet of the condenser above the pump centre line.

If M_p and M_f are the masses of water in lb. per second, passing through the partial and final condensers respectively,

Then $M_p + M_f = 20{\cdot}9$ lb. per second.

Then $$\frac{62{\cdot}3}{144}\left(\frac{12{\cdot}56 \times 84}{20{\cdot}9} + \frac{7{\cdot}07 \times 45}{M_p} + \frac{220}{M_p}\right) = 34 \text{ seconds.}$$

Weight of cooling water through partial condenser

$$= 15{\cdot}7 \text{ lb. per second or } 56{,}600 \text{ lb. per hour} \quad . \quad . \quad (16)$$

$\therefore$ Weight of cooling water through final condenser

$$= 5{\cdot}2 \text{ lb. per second or } 18{,}700 \text{ lb. per hour} \quad . \quad . \quad (17)$$

Specifications of Residue, Product and Tops Distilled.

	Residue.	White Spirit.	Tops.
Sp. Gr. (60/60° F.) . . .	0·813	0·7855	0·7715
Flash Point (Abel) . . .	—	98° F.	—
A.S.T.M. Distillation (Barometric Pressure, 780 mm. Hg.)—			
	°C.	°C.	°C.
I.B.P.	196·5	156·0	131·0
10%	200·5	160·0	137·5
20%	201·5	161·5	140·0
30%	202·5	163·0	142·0
40%	203·5	164·5	143·5
50%	205·0	166·0	145·0
60%	206·5	167·5	147·0
70%	208·0	169·5	148·5
80%	211·0	172·0	151·0
90%	216·0	175·5	154·5
F.B.P.	242·0	188·0	161·5
Recovery	99%	99%	99%

Part III.—CALCULATIONS ON PLANT.

Heat Tables used :—

Steam.—Enlarged Callendar Steam Table.

Oils.—Pub. No. 97 U.S.A. Bureau of Standards.

When dealing with a continuous plant of this description and size, it is the usual practice to compute balances of materials and heat on the basis of arithmetic averages. This has already been done in the case of materials, and any lack of coincidence placed against "losses." In the case of temperatures, it will be seen that the conditions of the plant at noon may be taken to form quite a good mean, so that these values are taken without further alteration.

The relevant figures are :—

	lb. per hour.
Throughput of crude	4920
	°C.
Inlet temperature of crude to plant	5
Intermediate temperature between preheaters	137
Temperature of crude to first column	137
,, bottoms of No. 1 column	155
,, recirculated bottoms to No. 1 column	162
,, vapours to No. 2 column	129·5
,, bottoms of No. 2 column	104
,, vapours to partial condenser	97
,, vapours to final condenser	94
,, benzine ex final condenser	13
,, product ex heat exchangers	34

	lb. per hour.
Production of residue	40
,, product	3940
,, tops	920

Residue/Crude Heat Exchanger.—Not in use continuously.

Product/Crude Heat Exchanger.—On the outside of this heat exchanger is pumped the product from No. 2 column, containing a portion of water. A slight amount of gassing or vaporisation takes place on the suction side of the draw-off pump, due to the very slight and pulsating release in pressure occurring. However, it is safe to assume that the positive pressure on the delivery side of 10–15 lb. gauge is sufficient to recondense any such small amount of vapour.

Recent alterations around the base of the plant have necessitated the removal of a part of the lagging of the suction and delivery lines of this pump, and the insulation had not then been replaced : a certain drop in temperature, therefore, takes place before entry to the heat exchanger, which, by rough measurement, is of the order of 5° C. This figure is taken.

Inlet temperature of product and water	99° C.
Outlet temperature of product and water	34° C.
Amount of spirit	3940 lb. per hour.
Amount of water	400 lb. per hour.
Heat gained by crude (allow 5 per cent. heat loss).	$2{\cdot}58 \times 10^5$ B.Th.U. per hour.
Amount of crude	4920 lb. per hour.
Heat gained by crude.	54 B.Th.U. per lb.
Inlet temperature of crude	5° C.
Outlet temperature of crude	66° C.

Steam Preheaters.—It will be observed that the inlet temperature to the second is the same as, and on occasions exceeds, that of the outlet, although 222,000 B.Th.U. per hour (cf. 14) are being absorbed by it. Process steam is injected into the inlet of the first preheater. The pressure on the crude at this point—about 20 lb. per sq. in. gauge—is sufficiently high to inhibit the formation of much vapour. The pressure in the cross-over line between the two preheaters is then roughly 10 lb. per sq. in. gauge, and the amount of vaporisation occurring cannot be estimated without special apparatus. The outlet pressure to the column can be taken as substantially that of the column itself at that point—*i.e.*, roughly the mean between the bottoms of Nos. 1 and 2 columns.

It would be better, therefore, to consider the two preheaters as one, as then the amount of vaporisation after the first vessel is left out of account; however, the amount of vapours leaving the second preheater must be known, and two methods present themselves:—

1. By a heat balance of the preheater. This is quite straightforward and requires no comment, except it should not be forgotten that a 1 per cent. difference in the calculated value of the heat loss will alter the calculated amount of vapours evolved by about 3 per cent.
2. By consideration of the partial pressure of the steam in relation to the temperature of outlet. The following assumptions will be made:—

   (*a*) That the pressure at the outlet of the last preheater is sensibly that of the point of inlet to the column. A short 4-in. pipe intervenes, therefore the difference is negligible.

   (*b*) That sufficient time is available for the inter-diffusion of the steam and hydrocarbon vapours, or, what amounts to the same, a degree of equilibrium must be postulated. Little information is available on this point, but experience with other and similar plant would indicate that "saturation" approaches equilibrium.

   (*c*) That the latter half of an A.S.T.M. distillation curve corresponds to the similar portion of a True Boiling-point analysis.

   (*d*) That the relationship between the vapour pressure and temperature of the crude is specified by the curve of a pure hydrocarbon of molecular weight agreeing with the mean molecular weight of the crude. Actually this crude has an A.S.T.M. boiling range at atmospheric pressure of about 50° C., and will not conform exactly to a pure hydrocarbon. The resulting error will be approximately 10 per cent. too high.

Method 1.

Inlet temperature of crude to preheaters	66° C.
Outlet temperature of crude from preheaters	137° C.
Sensible heat absorbed by crude	70 B.Th.U. per lb.
Latent heat absorbed by crude	109 B.Th.U. per lb. evaporated.
From (1) Amount of crude processed	4920 lb. per hour.
From (6) Amount of process steam	860 lb. per hour.
Heat in process steam at point of entry	1223 B.Th.U. per lb.

It will be shown later that the partial pressure of the steam under equilibrium conditions = 400 mm. (7·75 lb. per sq. in.).

∴ Amount of heat in process steam at outlet . . 1203 B.Th.U. per lb.
From (13 and 14), heat supplied by steam . . $7{\cdot}00 \times 10^5$ B.Th.U. per hour.

Let x = fraction of crude vaporised.
Assume 5 per cent. of the heat in the heating steam is lost—

$$7{\cdot}00 \times 10^5 \times 0{\cdot}95 + 860(1223 - 1203) = 4920(70 + 109x).$$

Whence $x = 0{\cdot}624$ . . . . . (18)

Method 2.

A Venezuelan distillate of sp. gr. 0·7855 has a molecular weight of 120, very nearly,* from which it may be calculated that the partial pressure on the spirit is 400 mm. According to the assumptions already made, at this pressure and a temperature of 137° C. the spirit is under equilibrium conditions, and corresponds to a pressure of 760 mm. and 165° C.

From the A.S.T.M. distillation curve 60 per cent. is vaporised at this temperature. This is in quite good agreement with the result obtained by heat balance.

In Method 1, the heat loss from the preheaters has been provisionally fixed at $3{\cdot}5 \times 10^4$ B.Th.U. per hour. It will be seen that 5 per cent. heat loss is assumed, and precedence for this is found in past usage. It includes not only radiation and convection, but also possible error of sensible and latent heat charts, as well as any shortcomings of steam traps. The radiation and convection losses can be calculated thus :—

The mean total area lagging of both preheaters = 46 sq. ft. The insulation is composed of plastic 2 in. thick magnesia and magnesia mattresses, and the conductivity may be fixed at 0·58 B.Th.U. per sq. ft. per hour per 1 in. per 1° F. temperature difference.

With an internal temperature of 137° C., and taking the emission constant as unity and convection as 0·34,† the rate of heat loss is roughly 70 B.Th.U. per sq. ft. per hour.

However, no allowance has been made for the exposed portions of flanges of the covers, which are left exposed owing to the danger of spontaneous combustion in asbestos wool, should a flange leak spirit. Such unlagged surface, in a relatively small area, will cause a considerably higher heat loss, and one difficult to calculate, especially with the inclement weather prevailing.

The heat losses are 3200 B.Th.U. per hour, or one-tenth of the value taken. The balance is assumed to be due to the inaccuracies in the latent heat chart, and on account of errors arising in the steam traps.

Heat Balance of Bottom Reheater.

Inlet temperature of bottoms to heater	155° C.
Outlet temperature of bottoms from heater	162° C.
Gain in sensible heat in bottoms	8 B.Th.U. per lb.

In view of the slight increase in temperature in the heater, the small pressure rise after the centrifugal pump (about 2 lb. per sq. in.) may be

* *J.I.P.T.*, 1932, **18**, 852.
† "The Calculation of Heat Transmission," Fishenden and Saunders.

taken as being sufficient to prevent any appreciable vaporisation, especially as there is no live steam present.

From (15) heat absorbed from heating steam $1{\cdot}84 \times 10^5$ B.Th.U. per hour.

As before, assuming 5 per cent. of this is lost,

Amount of circulation $= 2{\cdot}28 \times 10^4$ lb. per hour (53 galls. per min. approx.).

Heat Balance of No. 1 Column.

Amount of heat in feed (137° C.)	=	4920 (128 + 0·624 × 109).
	=	$9{\cdot}65 \times 10^5$ B.Th.U. per hour.
Amount of heat in process steam	=	860 × 1203 ,, ,,
Amount of heat in preheaters	=	$10{\cdot}35 \times 10^5$,, ,,
Amount of additional heat in recirculated bottoms	=	$1{\cdot}75 \times 10^5$,, ,,
Amount of heat in process steam injected in the bottom of No. 1 column	=	390 × 1223 ,, ,,
	=	$4{\cdot}87 \times 10^5$,, ,,
Total heat supplied to column	=	$26{\cdot}62 \times 10^5$,, ,, (19)

The heat lost to atmosphere is calculated thus:—

Specification of lagging	2 in.—85 per cent. Magnesia, ½ in. hardsetting compound, and finished with galvanised steel sheeting.
Conductivity of mean temperature	0·66 B.Th.U. per sq. in. per hour per 1 in. per 1° F. mean temperature difference.
Surface area of insulation	532·5 sq. ft.
Total heat loss	$3{\cdot}5 \times 10^4$ B.Th.U. per hour.
Temperature of vapours from column	130° C.
Amount of spirit vapours	4800 lb. per hour.
Amount of steam	1250 lb. ,,

The radiation losses will cause a certain amount of reflux in the column. The actual amount of this reflux is immaterial, but it forms a basis for the statement that the vapours will not be "superheated."

Sensible heat in vapours (Sp. Gr. 0·780 at 60/60° F.).	116 B.Th.U. per hour.
Latent heat in vapours	111 ,, ,,
Total heat in vapours	$11{\cdot}1 \times 10^5$ B.Th.U. per hour.
Total heat in steam	$15{\cdot}0 \times 10^5$,, ,,
Sensible heat of residue	140 B.Th.U. per lb.
Heat in residue	$0{\cdot}056 \times 10^5$ B.Th.U. per hour.
∴ Total heat abstracted from column	$26{\cdot}506 \times 10^5$,, ,, (20)

STATEMENT.

Input.	B.Th.U. per hour.	*Output.*	B.Th.U. per hour.
Heat in feed	$9{\cdot}65 \times 10^5$	Heat loss	$0{\cdot}35 \times 10^5$
Heat in recirculator	$1{\cdot}75 \times 10^5$	Overhead vapours	$11{\cdot}1 \times 10^5$
Heat in live steam		Overhead steam	$15{\cdot}0 \times 10^5$
(*a*) in preheaters	$10{\cdot}35 \times 10^5$	Residue	$0{\cdot}056 \times 10^5$
(*b*) in bottom of column	$4{\cdot}87 \times 10^5$		
	$26{\cdot}62 \times 10^5$		$26{\cdot}506 \times 10^5$

Heat unaccounted for = 11,400 B.Th.U. per hour, or 0·43 per cent.

This satisfactorily small error in the calculations and allowances is the vindication of the procedure of taking as a basis for the radiation and unaccounted heat loss an amount for small vessels of 5 per cent. of the heat supplied.

Column No. 2.

Heat Balance.

Heat Supply—

		B.Th.U. per hour.
From (20)	Heat supplied to No. 2 column in the form of both spirit and steam vapours	$= 26{\cdot}100 \times 10^5$

Heat Removal—

	Radiation loss, assuming the same conductivity factor as before	$0{\cdot}234 \times 10^5$
From (4)	By white spirit (temp. 104° C.) . . .	$3{\cdot}74 \times 10^5$
„ (3)	Heat in water	$0{\cdot}75 \times 10^5$
„ (8)	Heat in water from reflux head . . .	$0{\cdot}21 \times 10^5$
„ (9)	Heat in overhead steam (partial pressure 12 lb. per sq. in.)	$8{\cdot}52 \times 10^5$
„ (5)	Sensible heat in overhead vapours . .	$0{\cdot}78 \times 10^5$
	Latent heat in overhead vapours . .	$1{\cdot}10 \times 10^5$
	The heat extracted in the reflux condenser . . .	$= x$
Total heat removed from column		$15{\cdot}334 \times 10^5 + x$
∴ Heat removed in reflux condenser		$10{\cdot}77 \times 10^5$ (21)

Now the vapours, both steam and spirit, at the top of the column, in their passage through the reflux condenser, are cooled from 97° C. to 94° C. A certain amount is condensed, and giving up latent heat becomes reflux.

Let R = amount of reflux of spirit.

Amount of heat removed by condensing steam (latent heat 977 B.Th.U. per lb.) = $1{\cdot}04 \times 10^5$ B.Th.U. per hour (assuming the water draw-off syphon to be functioning satisfactorily)

∴ $123{\cdot}0\ R = (10{\cdot}77 - 1{\cdot}04) \times 10^5$

Whence R = 7910 lb. per hour . . . . . (22)

or a reflux ratio 8·60 . . . . . (23)

A check on the amount of heat withdrawn in the reflux condenser is provided by consideration of the cooling water in this condenser.

Rise in temperature of cooling water . . .	10·5° C.
From (16) Weight of cooling water . . .	56,600 lb. per hour.
∴ Amount of heat abstracted	$10{\cdot}7 \times 10^5$ B.Th.U. per hour.

which is in good agreement with (21).

This, however, should be regarded more as a matter of luck than good measurement, nor does it imply accuracy in the latent heat chart. The very method of computing the weight of cooling water, and the comparatively small temperature rise, militate against an accurate estimate of the amount of reflux by this method.

(If the above figure of $10{\cdot}7 \times 10^5$ B.Th.U. per hour be taken as a basis for the calculation of reflux ratio, a negative heat loss in the column is obtained.)

Final Condenser.

	B.Th.U. per hour.	
Total heat in spirit vapours to condenser . . .	$= 1{\cdot}88 \times 10^5$	
Total heat in steam	$= 8{\cdot}52 \times 10^5$	
Total heat to condenser	$= 10{\cdot}40 \times 10^5$	
Heat in spirit leaving condenser (13° C.) . . .	$= 0{\cdot}08 \times 10^5$	
Heat in water leaving condenser (13° C.) . . .	$= 0{\cdot}21 \times 10^5$	
∴ Heat removed by cooling water	$= 10{\cdot}11 \times 10^5$	(24)
From (17) Rate of cooling water	18,700 lb. per hour.	
Initial temperature of cooling water	11° C.	
Final temperature of cooling water was estimated roughly at	40° C.	

∴ Heat absorbed = $10{\cdot}1 \times 10^5$ B.Th.U. per hour which is in good agreement with (24).

Calculations on Equipment.

It is proposed to touch lightly on this subject, and to work out only a few of the leading questions, such as heat transference factors and velocities of vapours. There are many other and interesting considerations which have only specialised value, and it is hoped that those who would delve further will find sufficient practical data to assist them.

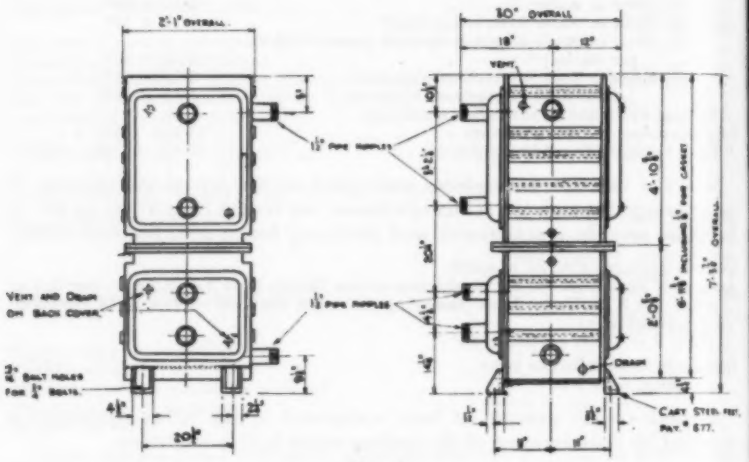

Fig. 3.

HEAT EXCHANGERS.

Heat Transfer Surface, 210 sq. ft.
Total number of Tubes, 744.
Length of Tubes, 18½ in.
Diameter of Tubes, ¾ in. O.D.
Material of Tubes, Admiralty metal.
Gauge of Tubes, 18.
Number of Passes through Tubes, 20-top, 4-bottom sect.
Average number of Tubes per Pass, 31.
Average area of Tubes per Pass, 10·34 sq. in.
Number of Passes outside of Tubes, 24.
Average Area of Passes outside of Tubes, 9 sq. in.

Heat Transfer Coefficients.—Product crude heat exchanger. Specification of equipment, see Fig. 3.

Heating surface	175 sq. ft.
Thus Velocity of crude	0·456 ft. per second.
Velocity of product and water	0·351
Heat transferred	$2·64 \times 10^{6}$ B.Th.U. per hour.
Inlet temperature of product and water	99° C.
Outlet temperature of product and water	34° C.
Inlet temperature of crude	5° C.
Outlet temperature of crude	66° C.
Postulating counter-current flow—	
Log mean temperature difference	30·5° C.
Heat transfer coefficient = 27·5 B.Th.U. per sq. ft. per hour per 1° F. M.T.D.	

First Preheater.—Specification, see Fig. 4. Heating surface, 70 sq. ft. In this vessel 860 lb. per hour of live steam is injected into the spirit inlet. The pressure at this point is about 25 lb. per sq. in. gauge and at the outlet from the preheater roughly 15 lb. per sq. in. gauge. The temperatures are 66° C. and 137° C. respectively. Under these conditions it is impossible to say what amount of vapour is present at any point of the

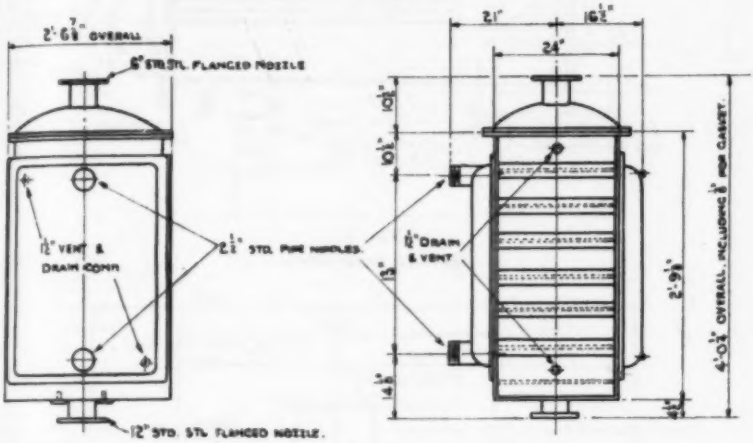

FIG. 4.

FIRST PREHEATER.

Heat Transfer Surface, 70 sq. ft.
Total number of Tubes, 248.
Length of Tubes, 18½ in.
Diameter of Tubes, ¼ in. O.D.
Material of Tubes, Admiralty metal.
Gauge of Tubes, 18.
Number of Passes in Tubes, 8.
Average number of Tubes per Pass, 31.
Average area of Tube Passes, 10·34 sq. in.
Number of Passes in Shell, 1.
Average area of Shell Passes, 102 sq. in.

tubes. At the outlet, it is assumed that no vaporisation obtains but that no steam has condensed, and the following calculations can be adopted :—

	Per second.
Volume of steam at 15 lb. per sq. in.	3·28 cu. ft.
Volume of oil at 15 lb. per sq. in.	0·285 cu. ft.
Thus Velocity of crude and steam	50 ft.
Velocity of steam outside tubes	0·623 ft.

Second Preheater.—Specification, see Fig. 5. Heating surface, 40 sq. ft. Taking the inlet spirit pressure of 15 lb. per sq. in. and the outlet of 4 lb. per sq. in. gauge, the maximum volume of vapours will occur at the outlet. The partial pressure of the steam at this point is 9·2 lb. per sq. in.

	Per second.
Volume of steam	10 cu. ft.
Neglecting volume of liquid—	
Velocity in tubes	250 ft.
Velocity of steam outside tubes	1·21 ft.

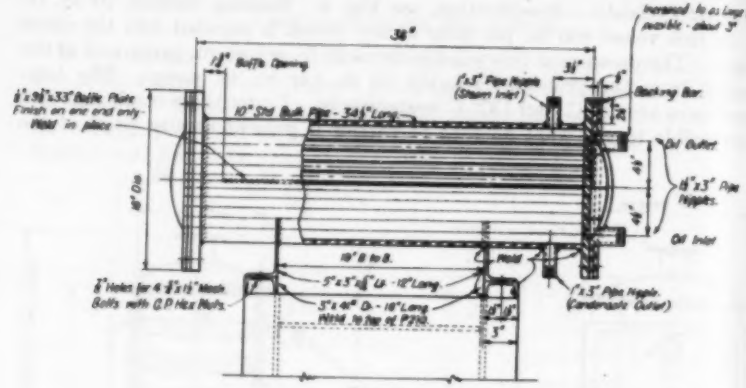

FIG. 5.

SECOND PREHEATER.

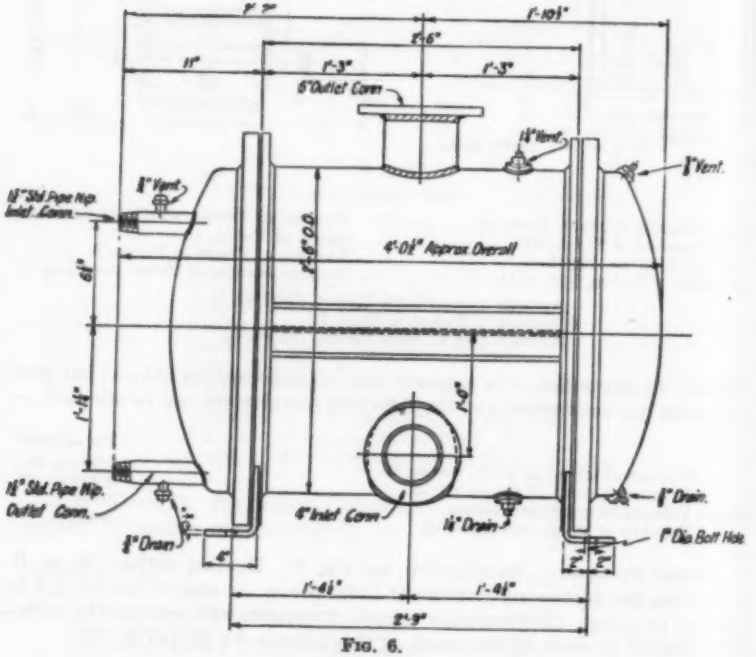

FIG. 6.

REHEATER.

Heat Transfer Coefficient of Combined Preheaters.—In this case it is not strictly accurate to take the logarithmic mean temperature to arrive at the temperature difference between the steam and the spirit.

Although more accurate methods are available for such cases, the ordinary log. mean temperature difference is generally taken for convenience, and is, therefore, adopted in these calculations.

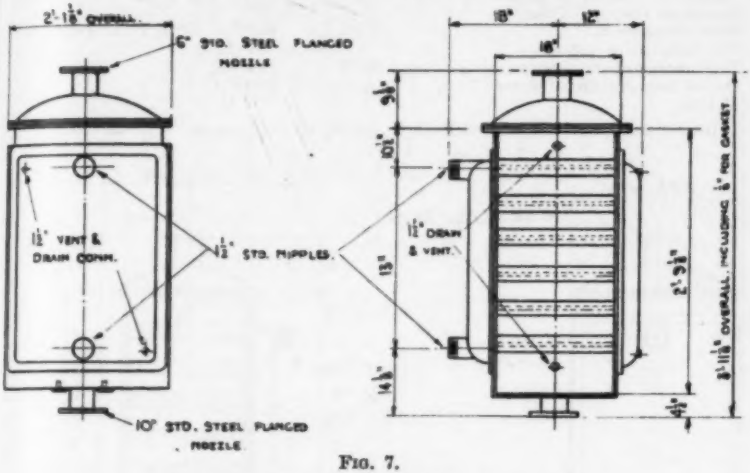
6" STD. STEEL FLANGED NOZZLE
1½" VENT & DRAIN CONN.
1½" STD. NIPPLES
10" STD. STEEL FLANGED NOZZLE
1½" DRAIN & VENT.
OVERALL, INCLUDING ½" FOR GASKET

FIG. 7.

PARTIAL CONDENSER.

Heat Transfer Surface, 120 sq. ft.
Total number of Tubes, 328.
Length of Tubes, 24½ in.
Diameter of Tubes, ¾ in. O.D.
Material of Tubes, Admiralty metal.
Gauge of Tubes, 18.
Number of Passes in Tubes, 8.
Average number of Tubes per Pass, 41.
Average area of Tube Passes, 13·8 sq. in.
Number of Passes in Shell, 1.
Average area of Shell Passes, 179·3 sq. in.

It may be as well to point out that the temperature of superheat in the heating steam is neglected. The heat due to superheat is only some 3 per cent. of the total, and, therefore, serious errors arise by taking the temperature of superheat into the calculation for mean temperature difference, actually in the present case about 15 per cent.

Inlet temperature of crude	66° C.
Outlet temperature of crude	137° C.
Temperature of heating steam	183° C. (neglecting superheat).
M.T.D.	76° C.

Heat transfer factor = 45 B.Th.U. per sq. ft. per hour per 1° F. M.T.D.

Reheater.—Specification, see Fig. 6.

Heat transfer area	210 sq. ft.
Velocity of recirculated bottoms, assuming no vaporisation	Unknown.
Velocity of heating steam outside tubes	0·93 ft. per second.
Heat transferred	5·45 × 10^6 B.Th.U. per hour.
Inlet temperature of bottoms	155° C.
Outlet temperature of bottoms	162° C.
Temperature of steam (saturated)	183° C.
M.T.D.	24·1° C.

Heat transfer coefficient = 60 B.Th.U. per sq. ft. per hour per 1° F. M.T.D.

Partial Condenser (*No. 2 Column*).—Specification, see Fig. 7.

Heat transfer area	120 sq. ft.
Velocity of water	2·62 ft. per second.
Maximum velocity of vapour	6·17 ,, ,,
Minimum velocity of vapour	5·5 ,, ,,
Heat transferred	10·77 × 10^5 B.Th.U. per hour.
Temperature of vapours	94° C.
Inlet temperature of water	11° C.
Outlet temperature of water	21·5° C.
M.T.D.	76° C.

Heat transfer coefficient = 65 B.Th.U. per sq. ft. per hour per 1° F. M.T.D.

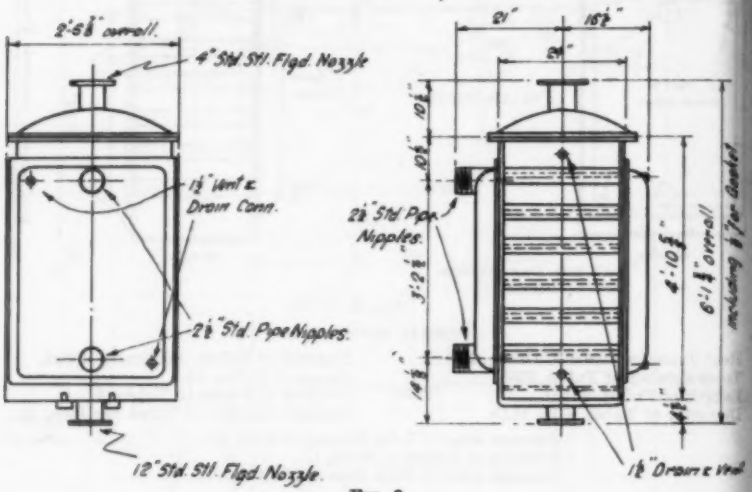

FIG. 8.

FINAL CONDENSER.

Heat Transfer Surface, 300 sq. ft.	Material of Tubes, Admiralty metal.
Total number of Tubes, 820.	Gauge of Tubes, 18.
Length of Tubes, 24½ in.	Number of Passes in Tubes, 20.
Diameter of Tubes, ⅝ in. O.D.	Average number of Tubes per Pass, 41.

Average area of Tube Passes, 13·8 sq. in.
Number of Passes in Shell, 1.
Average area of Shell Passes, 179·3 sq. in.

Final Condenser.—Specification, see Fig. 8.

Heat transfer area	300 sq. ft.
Velocity of water through tubes	0·87 ft. per second.
Maximum velocity of vapours outside tubes	5·38 ,, ,,
Heat transferred	10·54 × 10^5 B.Th.U. per hour.
Inlet temperature of vapour	93° C.
Outlet temperature of vapour	13° C.
Inlet temperature of water	11° C.
Outlet temperature of water	35° C.
M.T.D.	16° C.

Heat transfer coefficient = 122 B.Th.U. per sq. ft. per hour per 1° F. M.T.D.

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s, 41.

hour.